R-4646-1

THE PHENOMENOLOGY OF SYNERGISTIC CATALYZED PROPELLANTS

SECOND SEMI-ANNUAL TECHNICAL REPORT

1 NOVEMBER 1970 THROUGH 30 APRIL 1971

ONR CONTRACT N00014-70-C-0354

Rocketdyne
North American Rockwell

SOLID ROCKET DIVISION
P.O. Box 548
McGregor, Texas 76657

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CONTENTS

FIGURES

FIGURES

(Continued)

TABLES

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13. ABSTRACT

Report covers the second 6 months of a continuing study of the Keenan catalyst system that consists of a transition metal and a chloride. Initial DSC experiments produced some results that contradicted those of Keenan, but micro DTA experiments tended to confirm his results. DTA work was confined to isothermal work with glass-covered thermocouples. The TGA was used primarily in the isothermal mode at several temperatures to study the relative rates of decomposition. The DSC was used to study the AP catalyzed system, both as oxidizer/catalyst samples and as micromix propellant samples. Data from 11 batches of ammonium nitrate extrudable propellants are presented, and methods by which they were obtained are described. Computer print-outs of a least squares fit of strand burning rate data are included. Strand burning rates continue to verify burning rate depression by chloride. Results obtained to date from this study support the theory that suppression of the burning rate of ammonium dichromate catalyzed propellants occurs in the condensed phase. Isothermal TGA showed no induction time with the synergistic decomposition catalyst and a relatively constant rate of decomposition at each temperature studied. It appears that the induction time observed by Keenan was actually a self-heating time, and it is likely that the nitrogen sparge that Keenan used to delay the induction time was actually only carrying heat away from the sample convectively so that the sample did not reach a high enough temperature to decompose rapidly. DSC and DTA work with micro samples have led to the conclusion that most of the heat release in the sample is in the gas phase and not the condensed phase.

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Ammonium Nitrate Propellants						
Differential Scanning Calorimeter						
Thermogravimetric Analyzer						
Thermogram						
Differential Thermal Analyzer						
Ammonium Chloride						
Ammonium Perchlorate Propellants						
Ammonium Dichromate						

INTRODUCTION

This report covers the second 6 months of a continuing study of the Keenan catalyst system. This catalyst consists of a transition metal and a chloride, which A. G. Keenan found to be synergistic for the catalysis of ammonium nitrate decomposition.[1] Initial DSC experiments produced some results that contradicted those of Keenan; however, micro DTA experiments tended to confirm his results.

Extensive use of the TGA during this reporting period resulted in a clearer understanding of the phenomenology of this catalyst system. The use of the TGA has also afforded an explanation of the difference between DSC and DTA results. Eleven propellant mixes were made, and burning rate data were obtained over a relatively wide pressure range. As in the previous report only representative thermograms are included.

EXPERIMENTAL APPROACH

The experimental approach has been continued essentially as described in the first 6-month report.[2] Work with the DTA was confined to isothermal work with glass-covered thermocouples. The TGA was used primarily in the isothermal mode at a number of different temperatures to study the relative rates of decomposition. The DSC was used to initiate the study of the AP catalyzed system, both as oxidizer/catalyst samples and as micromix propellant samples.

Samples for the ammonium perchlorate study were prepared from the melt samples described in the previous report. Ground melts were mixed with plant-ground AP (approximately 20 microns average particle size)

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[1] Keenan, A. G.: Mechanism of Reactions of Oxidizer, Contract Nonr-4008(07), May 1966.

[2] Sammons, G. D.: The Phenomenology of Synergistic Catalyzed Propellants, Semi-annual Technical Report, ONR Contract 00014-70-C-0354, R-4646, November 1970.

in a wig-l-bug mixer. Table 1 shows the composition of these mixtures. DSC thermograms for each sample are presented in Fig. 1 through 8.

TABLE 1

AP SAMPLE COMPOSITIONS

Sample Number	Weight Fraction*					Melt Number
	AN	AC	SC	AD	PD	
4B-12-16	0.1000					9A
5B-12-16	0.0998			0.0002		3B
6B-12-16	0.0967	0.0033				11A
7B-12-16	0.0998				0.0002	13A
8B-12-16	0.0965		0.0035			10A
9B-12-16	0.0962		0.0035		0.0002	14A
10B-12-16	0.0965	0.0033		0.0002		2B

*All samples contain 0.9 weight fraction of 20 micron AP

LEGEND: AN = ammonium nitrate
AP = ammonium perchlorate
AC = ammonium chloride
SC = sodium chloride
AD = ammonium dichromate
PD = potassium dichromate

Seven of the 11 batches of propellant were ammonium nitrate extrudable propellants mixed in a 0.7-gallon horizontal Baker-Perkins mixer. The other batches were castable ammonium perchlorate propellants mixed in a 1-pint vertical Baker-Perkins mixer. Strands of the nitrate propellant about 3/16 inch in diameter were extruded and cured at 88 degrees for 48 hours for burning rate studies. A short section of 0.5-inch rod was extruded, cured, cut into 1-inch lengths, and sliced on a microtome. Samples for the DSC were prepared by punching a disc with a No. 1 cork borer from a microtome slice about 0.25 millimeter thick. Strands of the castable perchlorate propellant were prepared by extruding the fluid uncured propellant into restrictor-coated drinking straws. The extruded nitrate strands were coated with methyl methacrylate before they were burned.

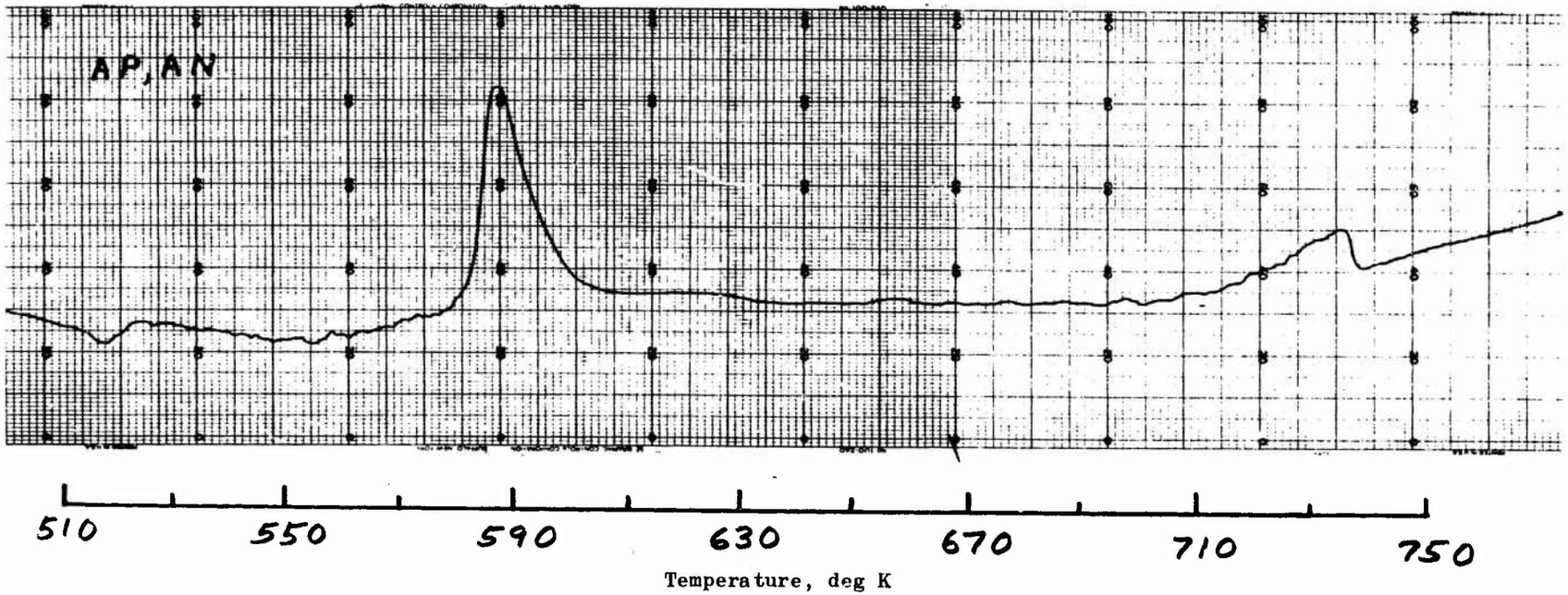

Figure 1. DSC Thermogram of AP Sample 4B-12-16 at 20 deg/min (Sample Weight 3.00 milligrams)

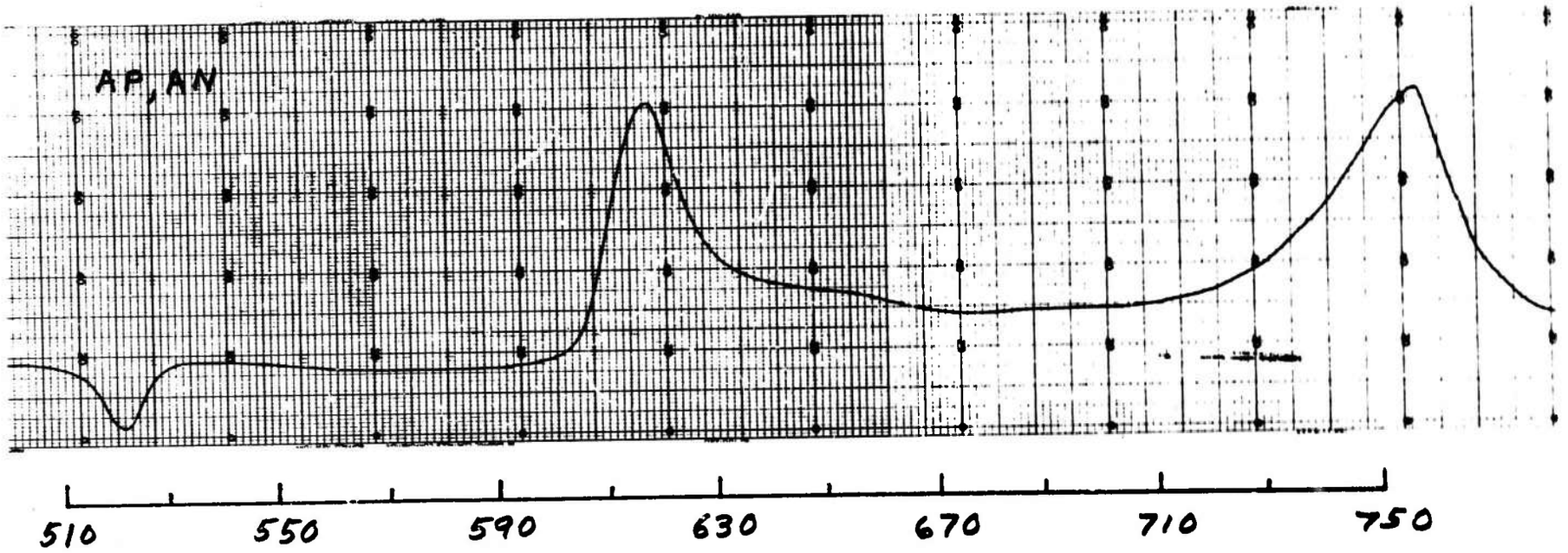

Figure 2. DSC Thermogram of AP Sample 4B-12-16 at 80 deg/min (Sample Weight 3.00 milligrams)

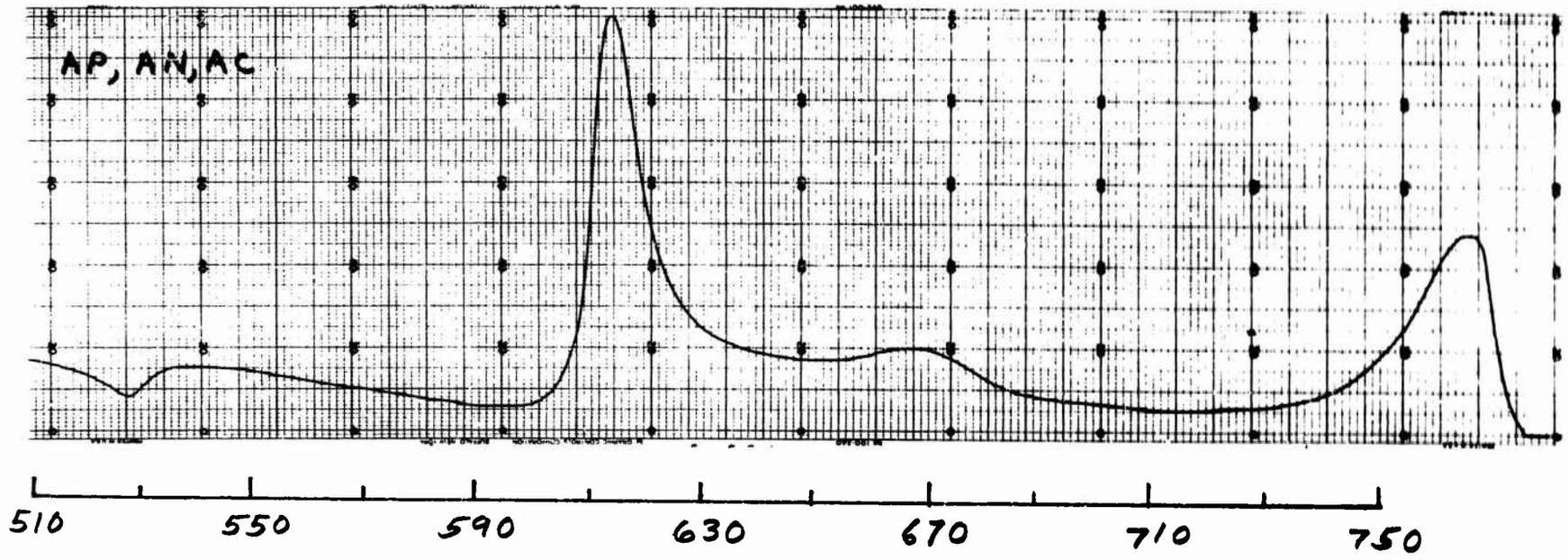

Figure 3. DSC Thermogram of AP Sample 6B-12-16 at 80 deg/min (Sample Weight 3.00 milligrams)

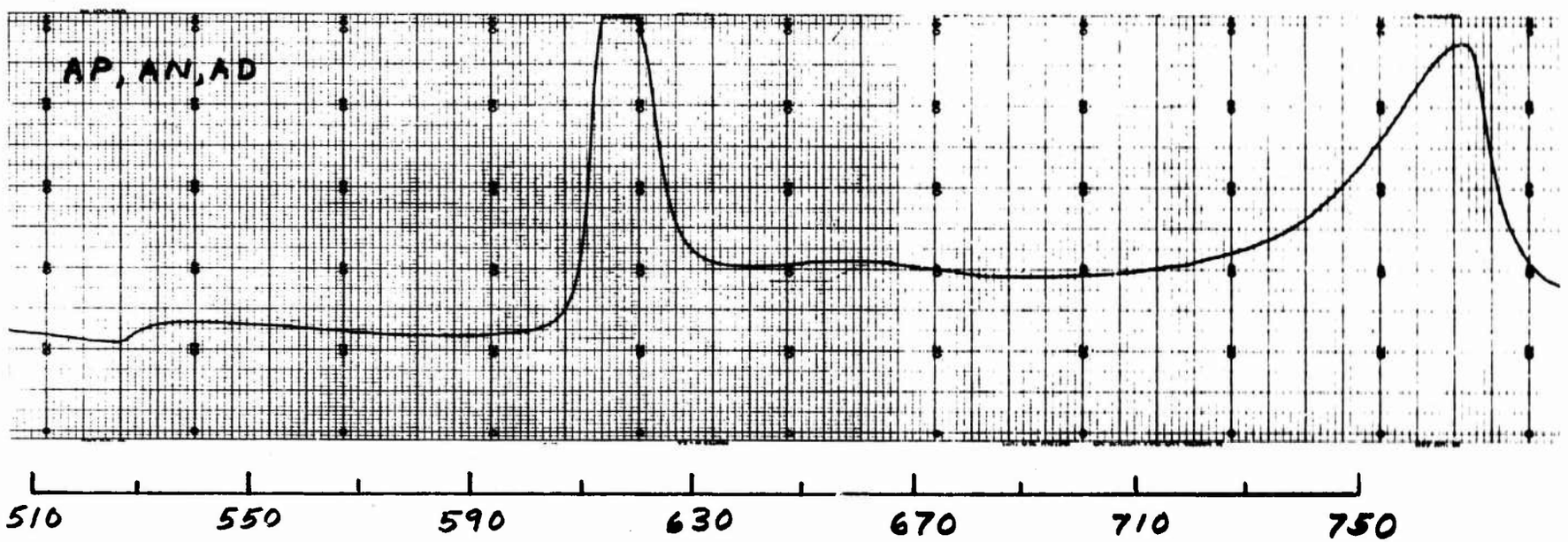

Figure 4. DSC Thermogram of AP Sample 5B-12-16 at 80 deg/min (Sample Weight 3.00 milligrams)

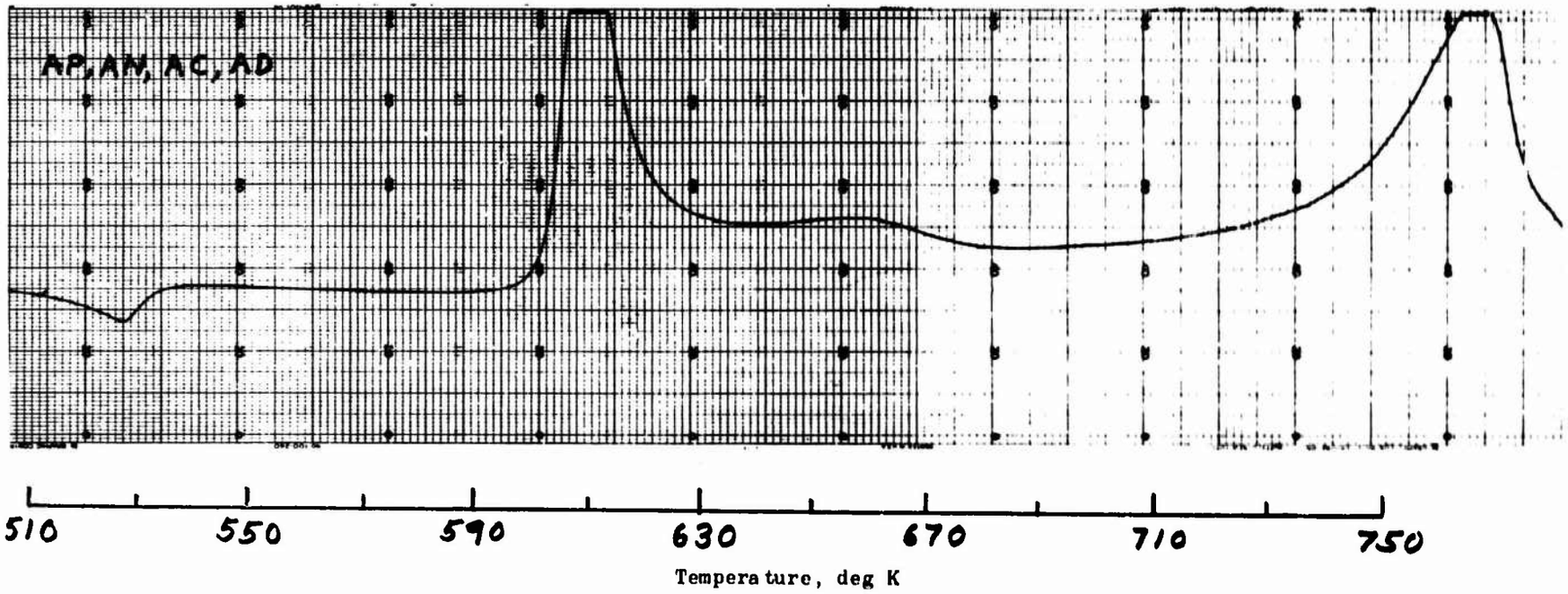

Figure 5. DSC Thermogram of AP Sample 10B-12-16 at 80 deg/min (Sample Weight 3.00 milligrams)

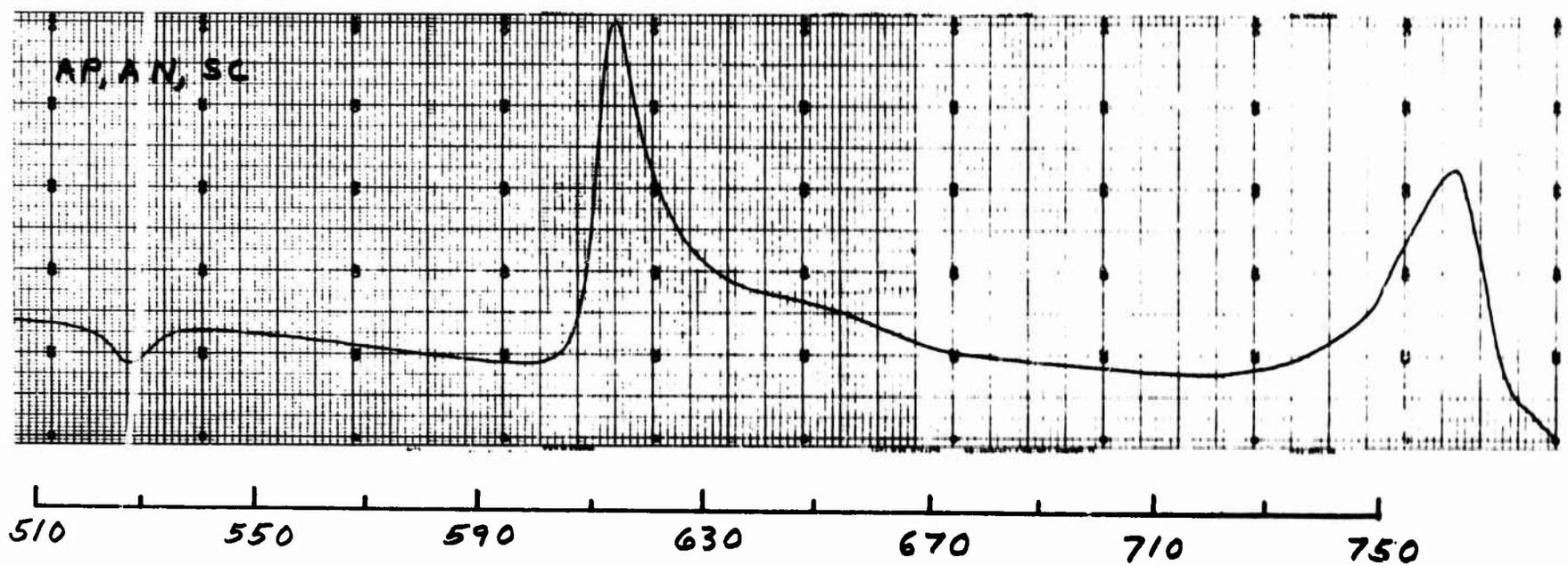

Figure 6. DSC Thermogram of AP Sample 8B-12-16 at 80 deg/min (Sample Weight 3.00 milligrams)

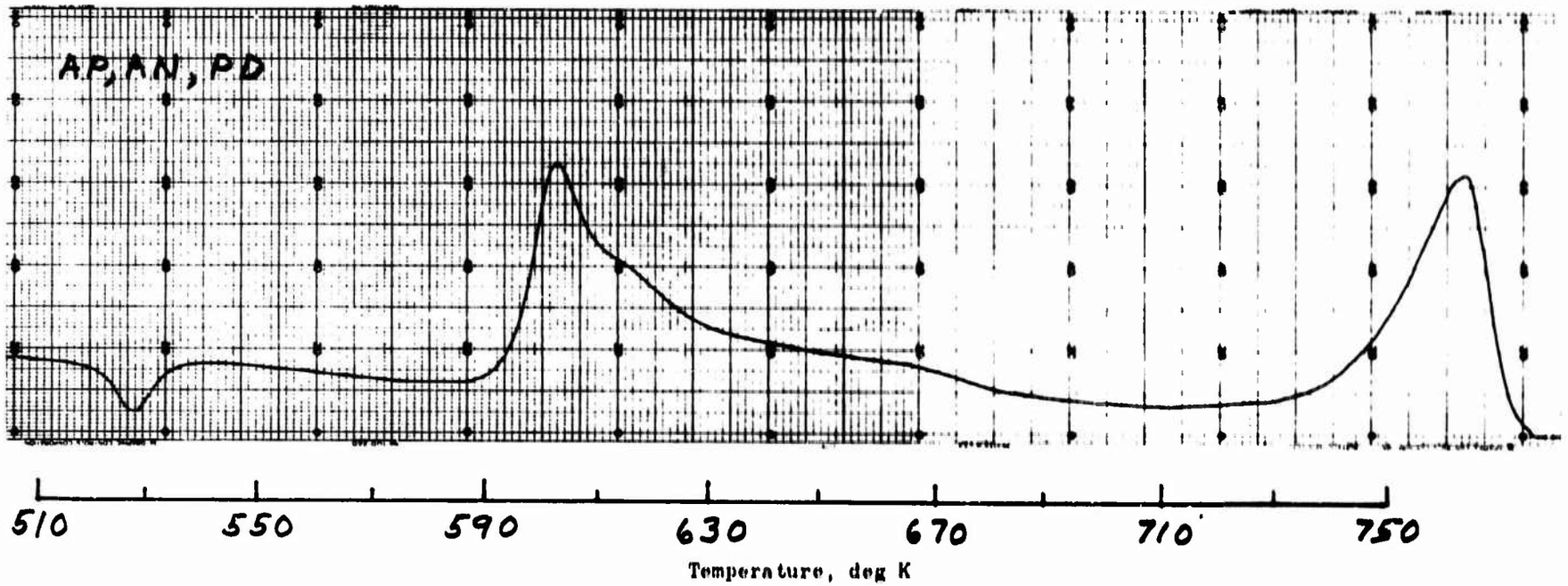

Figure 7. DSC Thermogram of AP Sample 7B-12-16 at 80 deg/min (Sample Weight 3.00 milligrams)

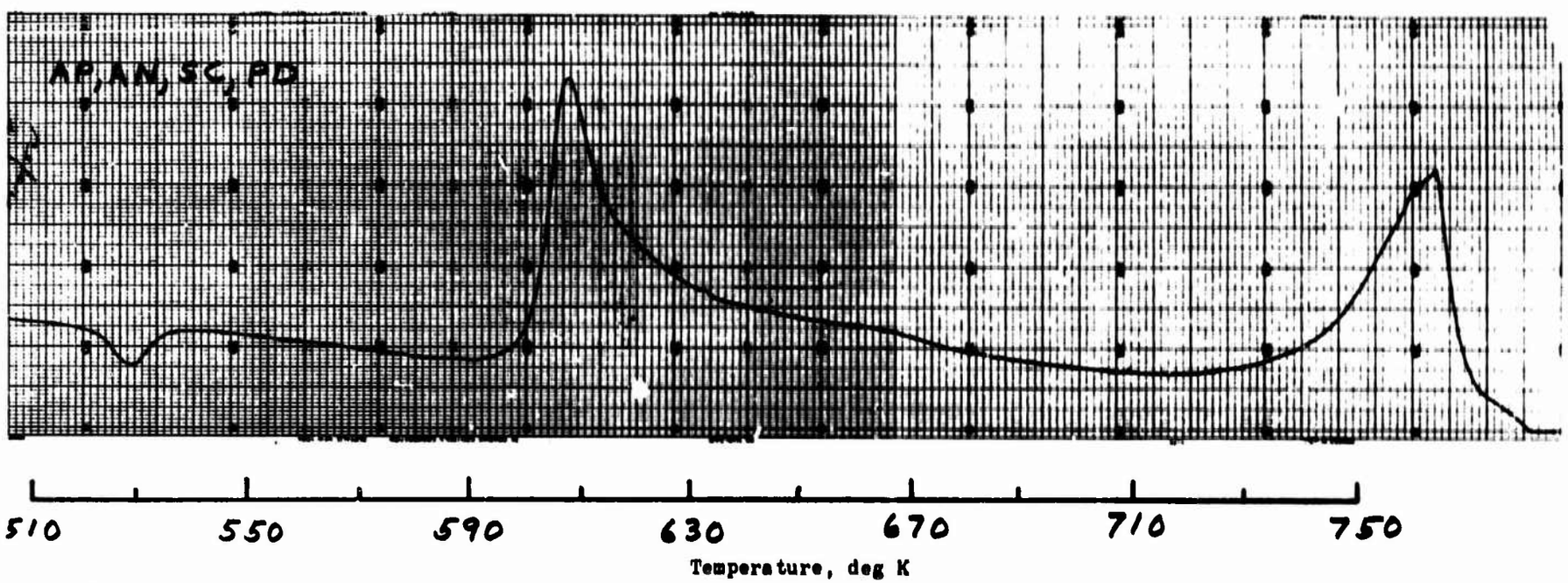

Figure 8. DSC Thermogram of AP Sample 9B-12-16 at 80 deg/min (Sample Weight 3.00 milligrams)

All strands were burned in 3-inch lengths in a standard Crawford bomb. Four replicates were burned at each of 200, 300, 500, 800, 1000, 1200, and 1500 psi nitrogen pressure.

ISOTHERMAL DTA

The duPont model 900 DTA was used in this study. All of the thermograms were run isothermally during this period and were made with thermocouples thinly coated with Pyrex glass.

The results obtained were surprising because in no case was an exotherm observed. Samples of about 20 milligrams were held at a number of temperatures from 195 to 250 C until the sample was completely decomposed. At present this can only be attributed to the difference in heat transfer due to the micro samples. Again, it appears that in the presence of the chloride, most of the exotherm is in the gas phase, as previously observed in dynamic runs.

DYNAMIC DSC (AP CATALYSIS)

Thermograms were run at 20 and 80 deg/min since it was found in previous studies that no reliable interpretations could be made without data from at least two scan rates. Comparison of Fig. 1 and 2 reveals that most information could be gained from the thermogram taken at 80 deg/min when AN/AP mixtures are being studied; apparently the presence of AN accelerates the sublimation of AP and almost all of the sample is gone before the high-temperature decomposition exotherm is reached.

Comparison of Fig. 2 and 3 shows very significant catalysis by ammonium chloride. Comparison of Fig. 4 and 7 indicates a better catalysis by ammonium dichromate than by potassium dichromate. This last assessment is based on the AP crystal phase change shown in the two figures; apparently ammonium dichromate lowered the activation energy more than the potassium salt. The near absence of an AP crystal phase

change in Fig. 4 is a sensitive indicator of an early exotherm, which means a low activation energy. This represents a good correlation with ballistic data since ammonium dichromate is known to be the best burn rate catalyst.

The special "Micromix" technique described in the last report was used to study the activity of the samples described in Table 1 in the presence of fuel. These samples have only been run at 20 deg/min thus far. Surprisingly, all of these micropropellants ignited at this heating rate. Based on the part of the curve obtained before ignition and the point of ignition, ammonium dichromate was again shown to be more effective than potassium dichromate (see Fig. 12 and 13). Sodium chloride and ammonium chloride again appeared to suppress the effect of chromium (see Fig. 9 to 13).

ISOTHERMAL TGA

A considerable number of isothermal thermogravimetric analyses were made in an effort to understand more fully the nature of the decomposition catalyst system being studied. These TGA thermograms were run as described in the last report with less than 3 minutes to equilibrium at the desired temperature. The upper curve in the example thermograms (Fig. 14 to 17) is a record of sample weight during the heat-up period and has temperature as the abscissa. When the desired temperature was reached the program was switched to isothermal and time base with 5 minutes per inch scale (30 seconds per small division). The distance from the zero abscissa to the start of the time base record indicates the time elapsed during heat-up. The encircled data represent temperature checks during the run.

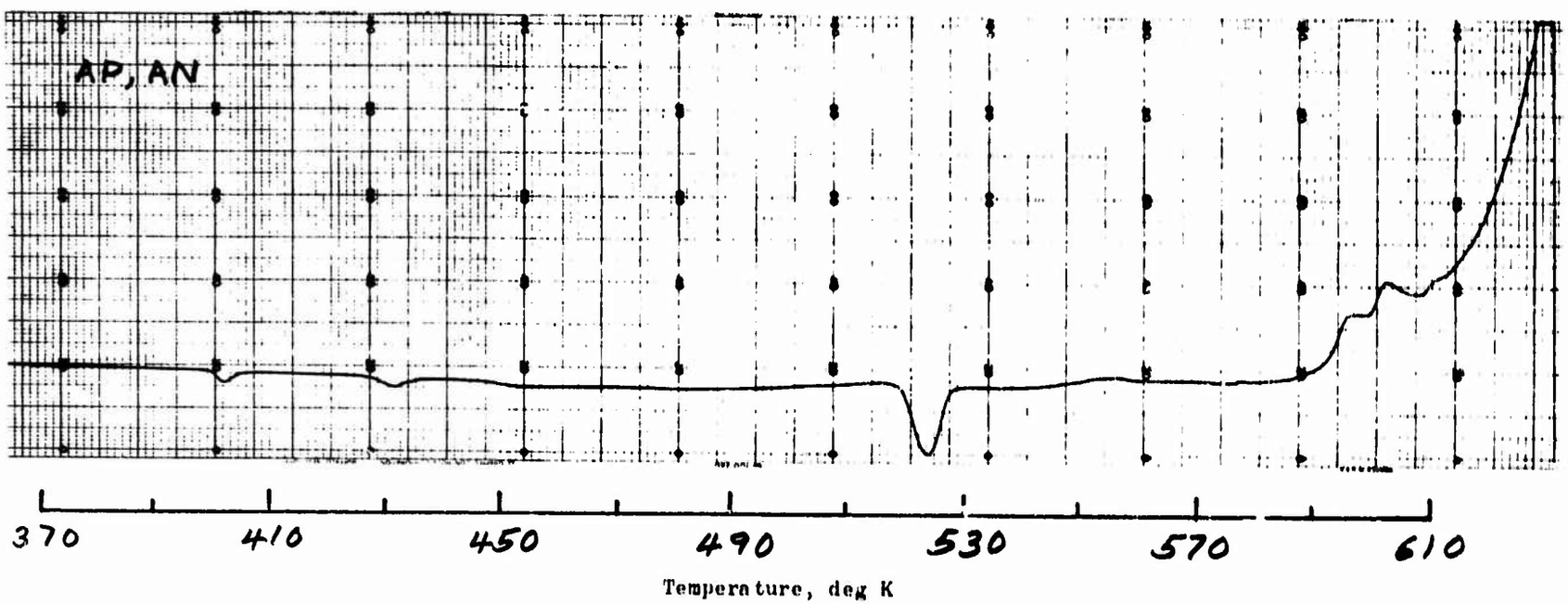

Figure 9. DSC Thermogram of Micromix Propellant of AP Sample 4B-12-16 at 20 deg/min (Sample Weight 3.00 milligrams plus 0.70 milligram Binder)

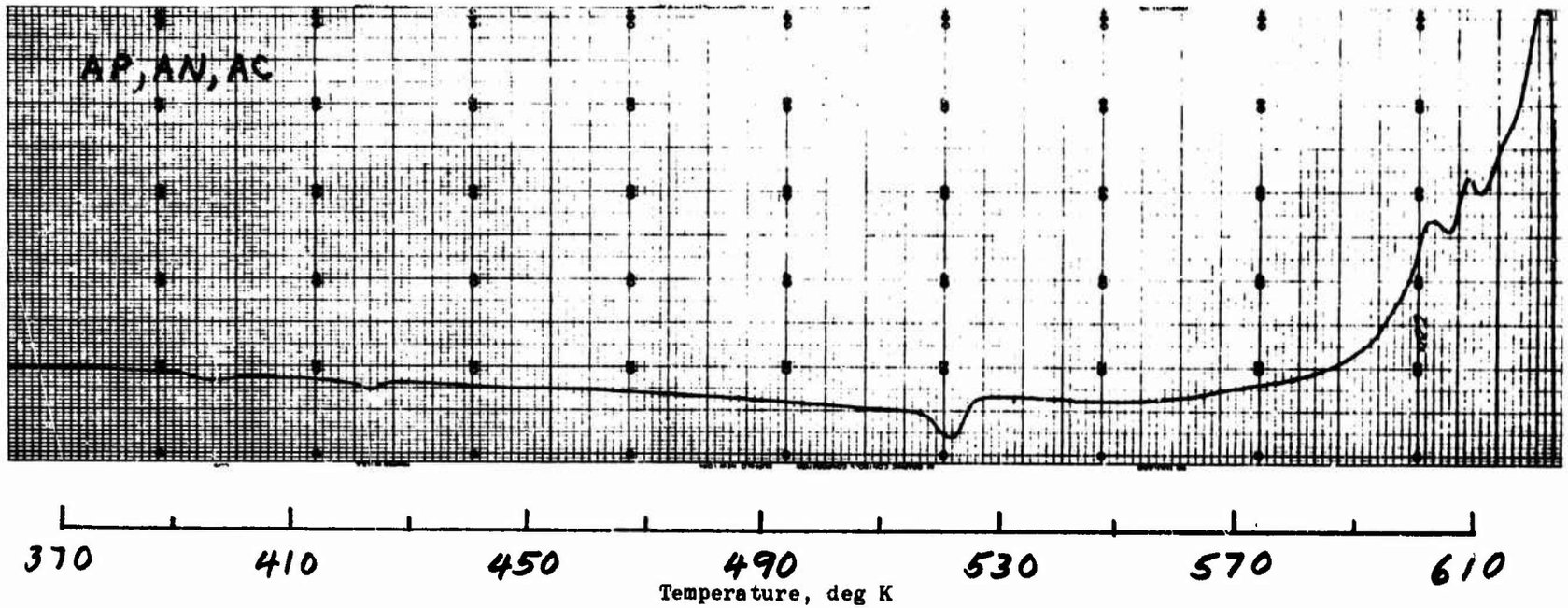

Figure 10. DSC Thermogram of Micromix Propellant of AP Sample 6B-12-16 at 20 deg/min (Sample Weight 3.00 milligrams Plus 0.59 milligram Binder)

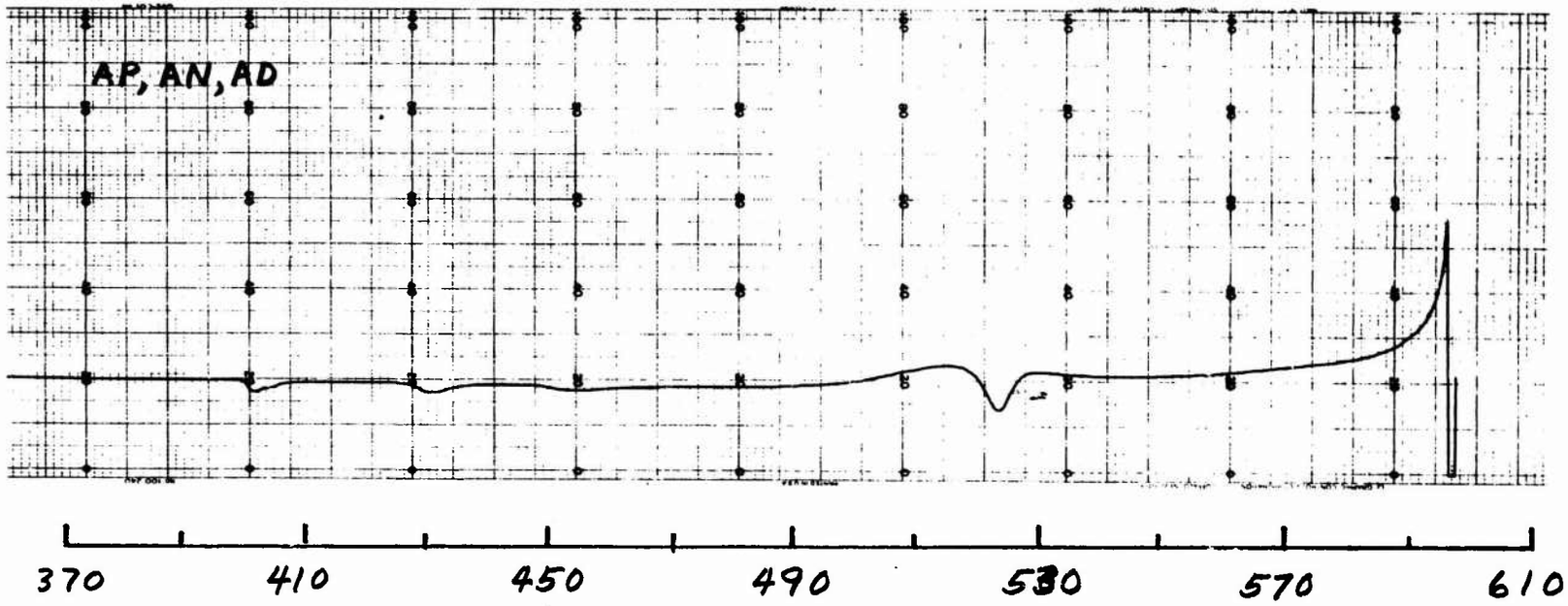

Figure 11. DSC Thermogram of Micromix Propellant of AP Sample 5B-12-16 at 20 deg/min (Sample Weight 3.00 milligrams Plus 0.62 milligram Binder)

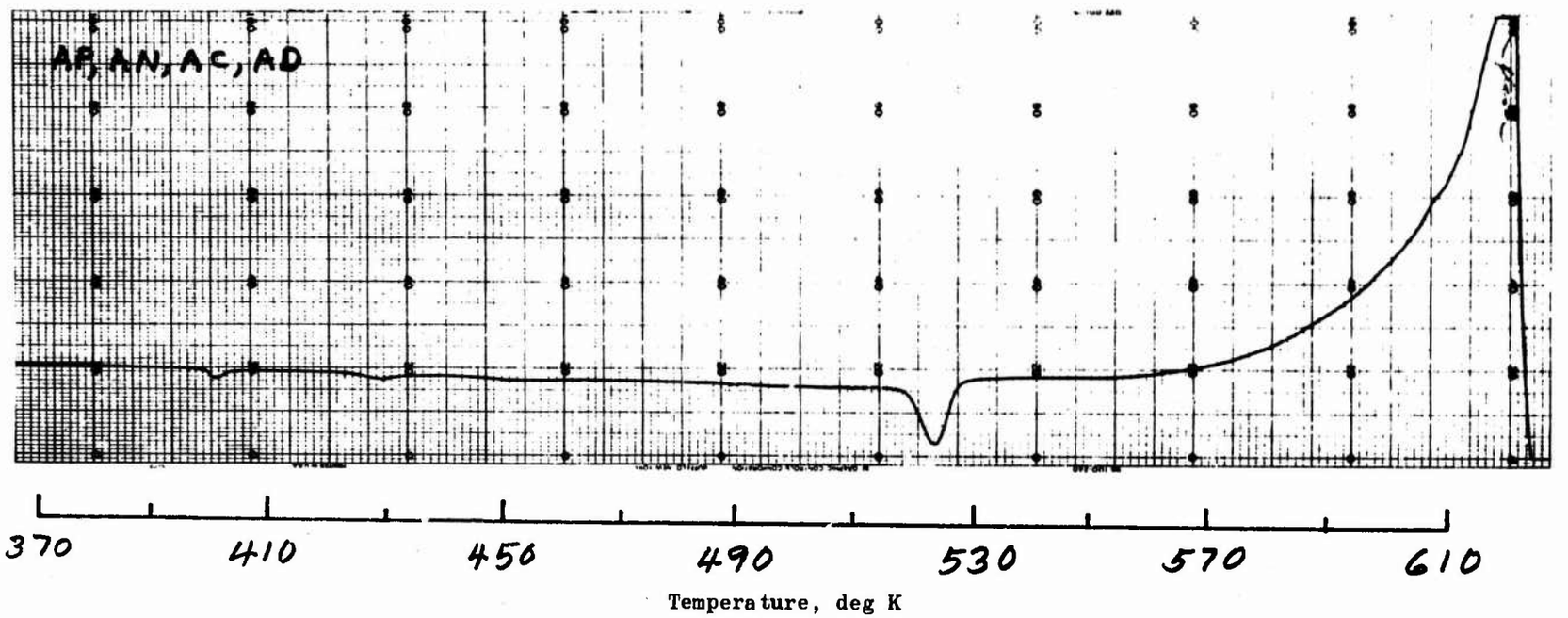

Figure 12. DSC Thermogram of Micromix Propellant of AP Sample 10B-12-16 at 20 deg/min (Sample Weight 3.00 milligrams Plus 1.12 milligrams Binder)

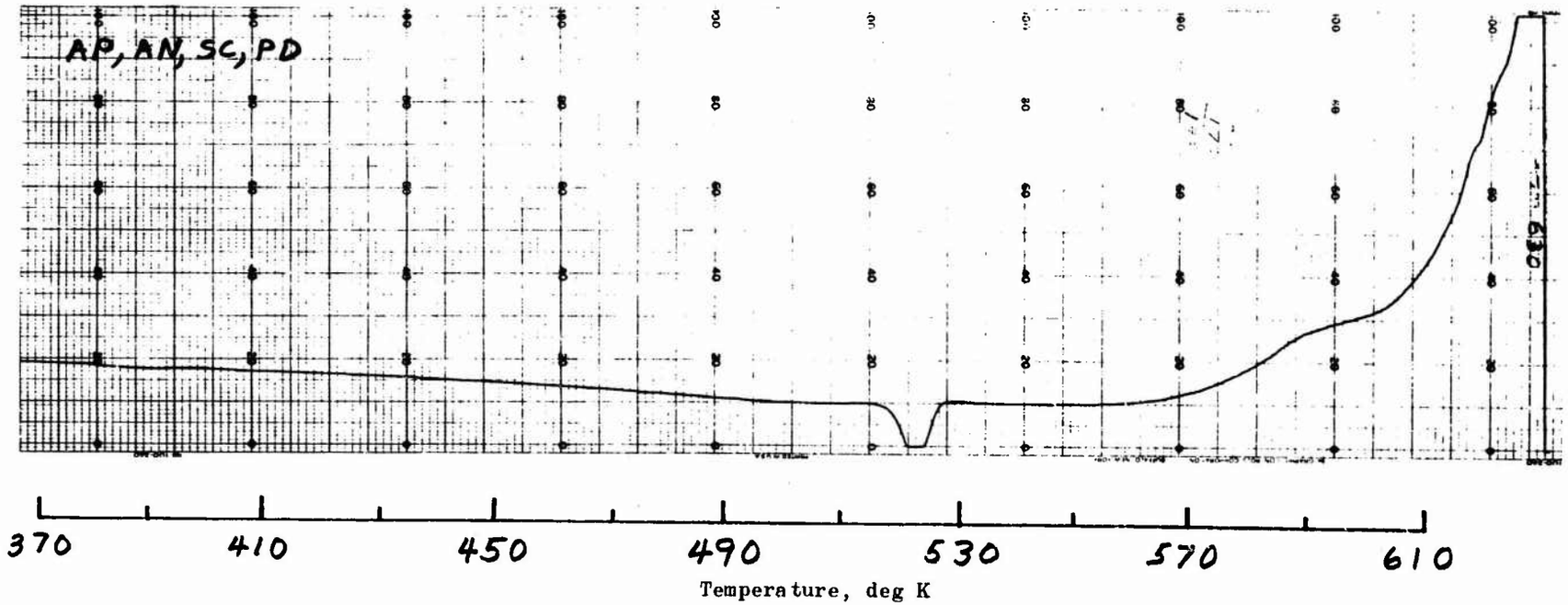

Figure 13. DSC Thermogram of Micromix Propellant of AP Sample 9B-12-16 at 20 deg/min (Sample Weight 3.00 milligrams Plus 0.58 milligram Binder)

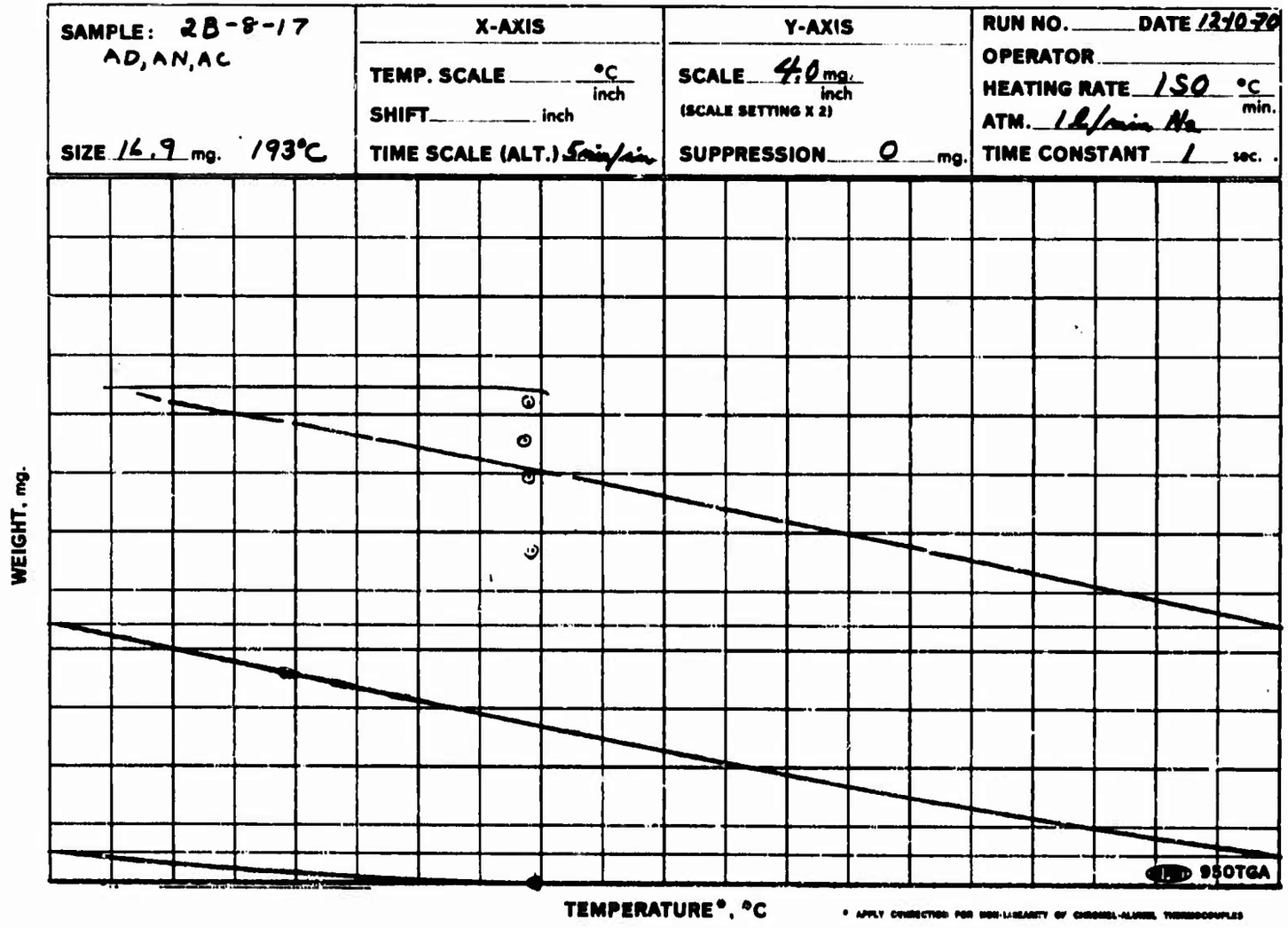

Figure 14. Isothermal TGA of Mix Sample 2B-8-17 at 193 C

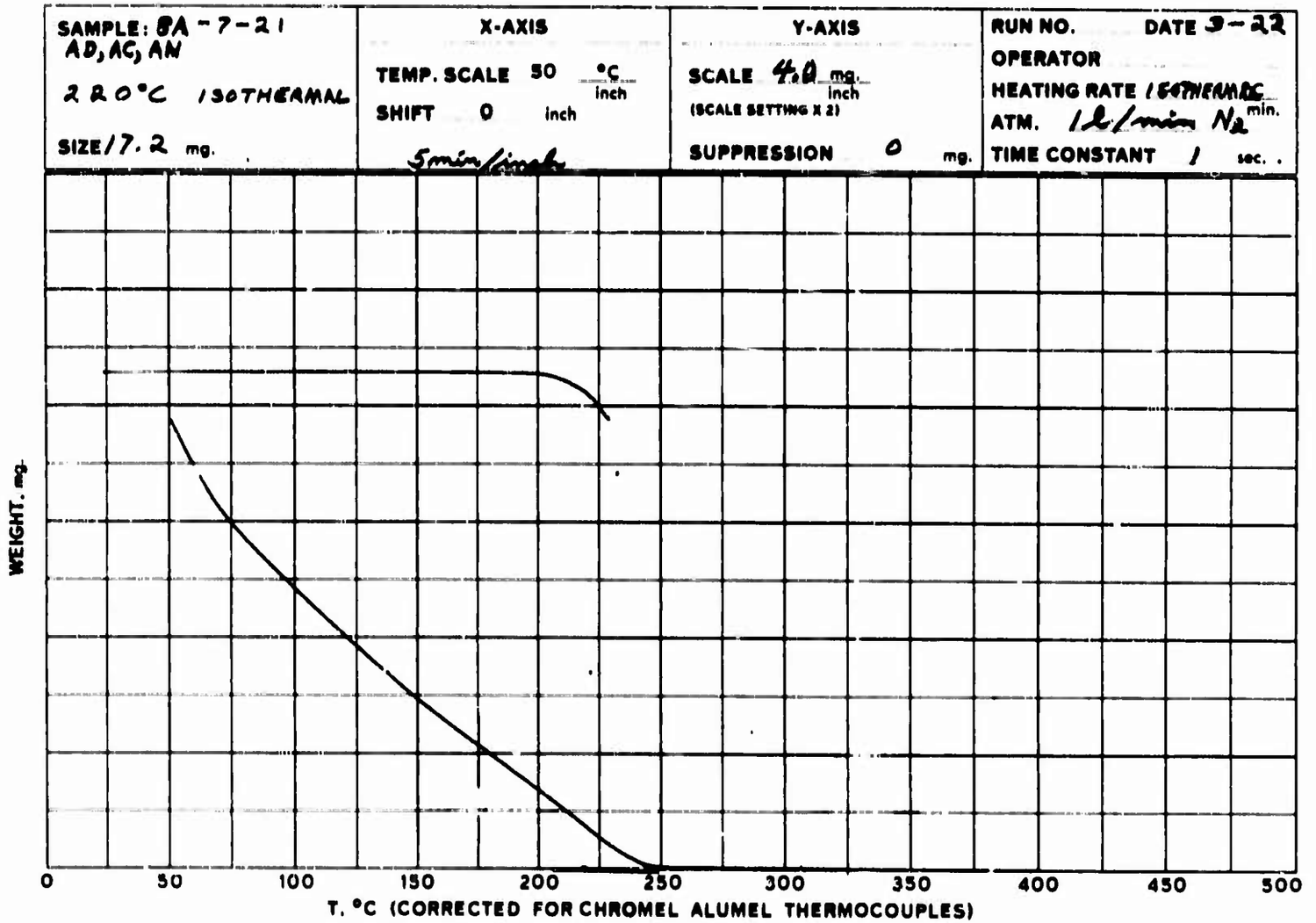

Figure 15. Isothermal TGA of Mix Sample SA-7-22 at 220 C

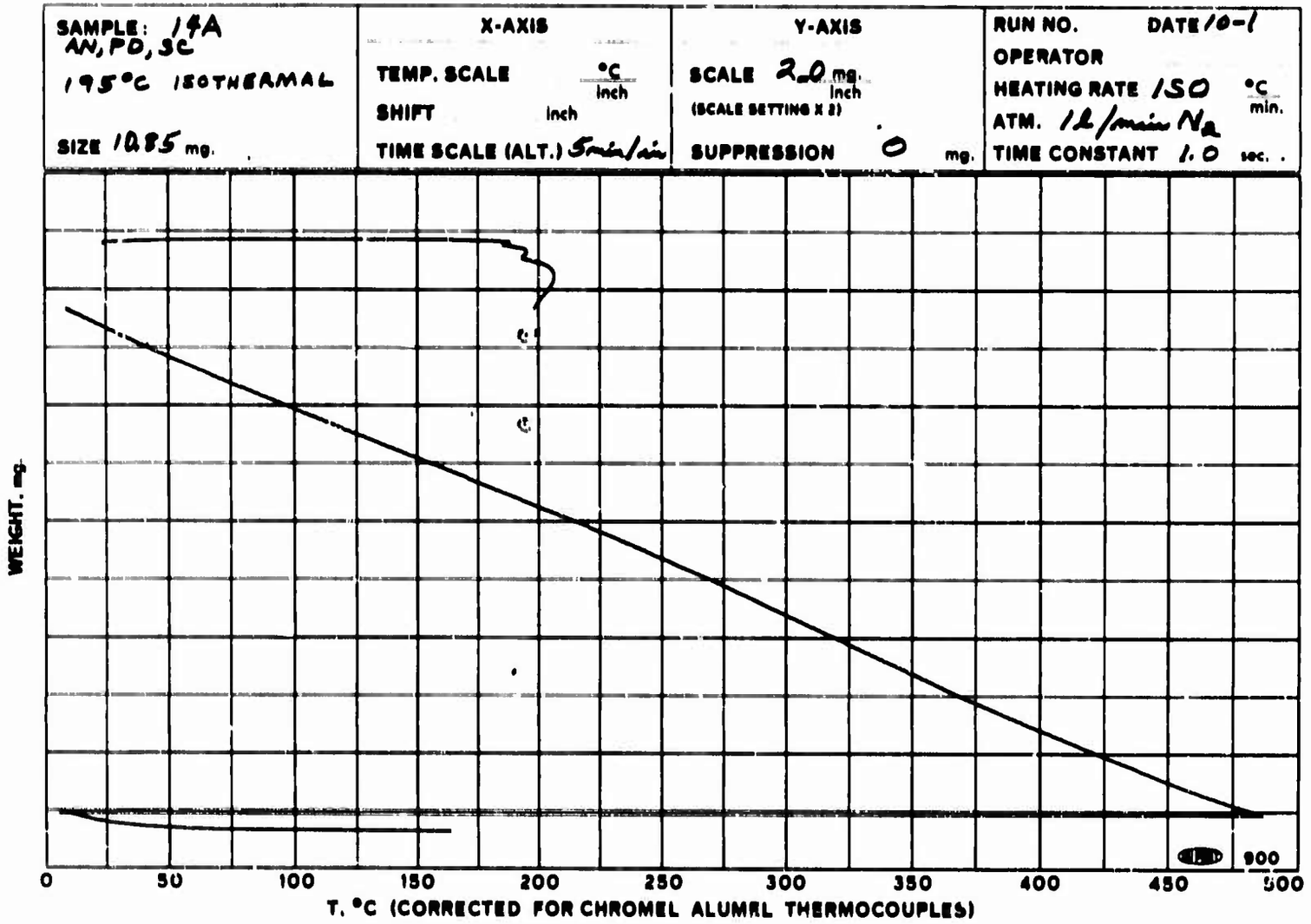

Figure 16. Isothermal TGA of Mix Sample 14A-7-30 at 195 C

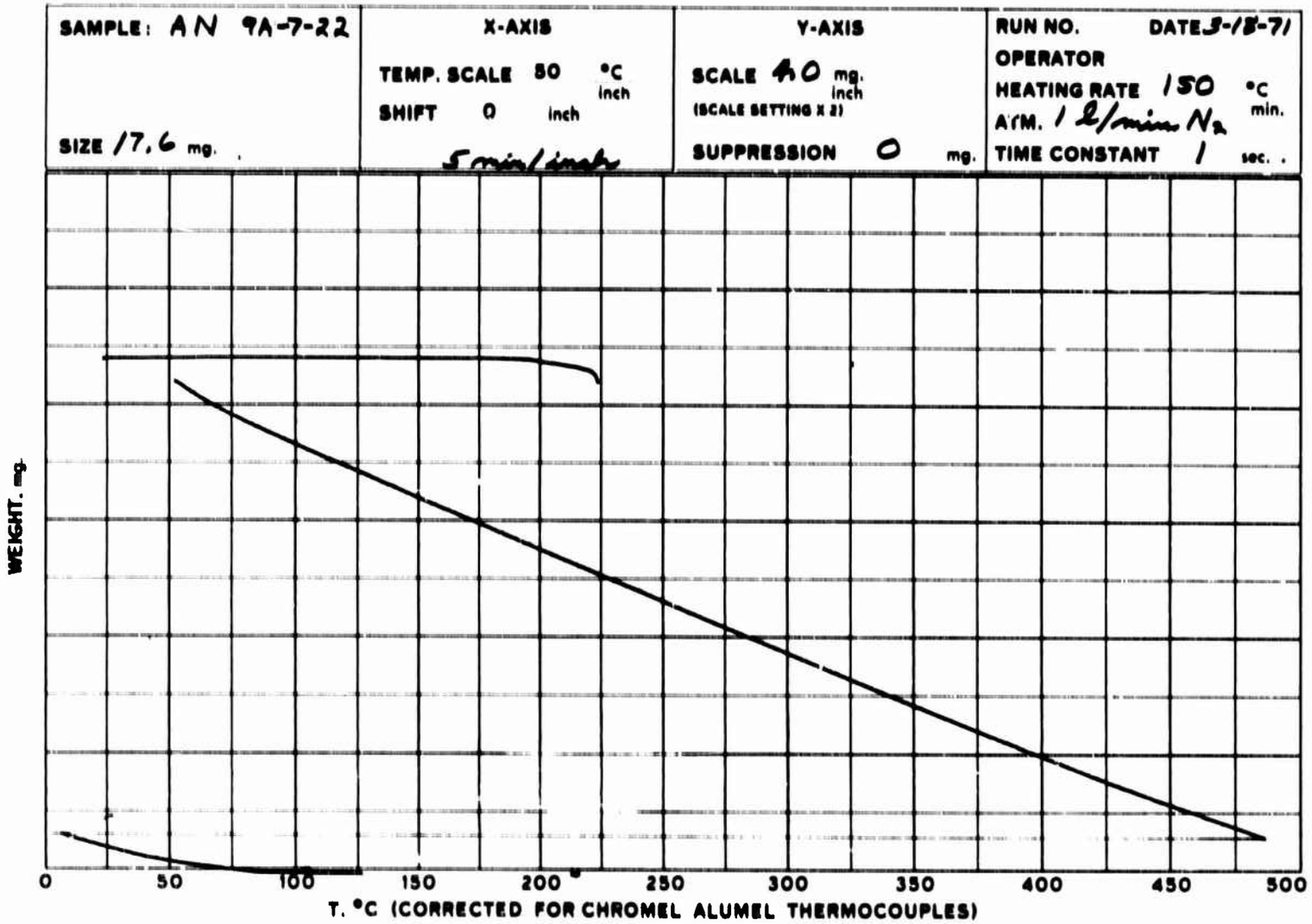

Figure 17. Isothermal TGA of Ammonium Nitrate Sample 9A-7-22 at 213 C

Keeman observed an induction time of over 60 minutes with the chromium/chloride catalyst system at 195 C furnace temperature. As shown in Fig. 15, no induction time was observed by TGA at 195 C; and, in fact, none was observed at any temperature above 195 C. In Fig. 15 decomposition started just before the sample reached 195 C and according to the time base recording the sample decomposed at an almost constant rate until it was totally consumed.

The rate constant of decomposition was obtained by calculating the slope of ln (weight) vs time. This gives a quantitative parameter for comparison purposes. Table 2 contains this data reduced from some of the isothermal runs. No attempt was made to least squares fit data or determine reaction order since kinetic parameters were not of particular interest in this program. First order kinetics were assumed so that a comparative parameter could be obtained easily.

TABLE 2

EFFECTIVE RATE CONSTANTS BY THERMOGRAVIMETRIC ANALYSIS FOR ISOTHERMAL DECOMPOSITIONS

Sample Number	Temperature, deg C	Rate Constant x 10^2, min^{-1}
14A-7-30 (AN, PD, SC)	187	1.75
	190	1.98
	195	1.59
	202	10.66
	205	11.71
	217	10.64
	220	12.27
9B-7-22 (AN)	195	2.77
	202	3.14
	218	3.96
11A-7-22 (AN, AC)	220	5.03
10A-7-22 (AN, SC)	214	4.86
8A-7-21 (AN, AD, AC)	218	6.75
2B-8-17 (AN, AD, AC)	193	2.18
Co-Crystallized (0.17% Cl)	195	2.38
	218	4.80
Co-Crystallized (12.0% Cl)	216	4.30

Table 2 indicates that a number of runs should be made to verify some of the values and clarify some of the trends. The most informative trends are given by sample 14A (AN, PD, SC) and 9B (AN). The effectiveness of the catalyst system with alkali metal salts is very pronounced. A significant increase in rate occurs around 200 C.

Sample 8A indicates the ammonium salts may be less effective as a decomposition catalyst than the alkali metal salts. More runs should be made with the AP salts. Comparing 11A and 10A with 9B (AN alone) indicates catalysis by sodium or ammonium chloride of about the same degree.

PROPELLANT MIXES (AMMONIUM NITRATE)

The composition of the seven batches of AN propellants made during this reporting period are listed in Table 3.

TABLE 3

COMPOSITION OF EXTRUDABLE AMMONIUM NITRATE PROPELLANTS

Propellant	Ingredients	Wt %	Actual Weight Used, grams
Control 1A	Binder	19.44	194.40
	Magnesium Oxide	0.54	5.40
	Ammonium Nitrate	79.86	798.60
	Ammonium Dichromate	0.16	1.60
			1000.00
Catalyzed 3	Binder	18.87	188.70
	Magnesium Oxide	0.52	5.20
	Ammonium Nitrate	77.51	775.10
	Ammonium Dichromate	0.58	5.80
	Sodium Chloride	2.52	25.20
			1000.00
Catalyzed 4	Binder	18.87	188.70
	Magnesium Oxide	0.52	5.20
	Ammonium Nitrate	77.51	775.10
	Ammonium Dichromate	0.58	5.80
	Ammonium Chloride	2.52	25.20
			1000.00
Control 5*	Binder	20.00	200.00
	Ammonium Nitrate	79.50	795.00
	Ammonium Dichromate	0.50	5.00
			1000.00
Catalyzed 5	Binder	19.47	194.70
	Ammonium Nitrate	77.41	774.10
	Ammonium Dichromate	0.49	4.90
	Ammonium Chloride	2.63	26.30
			1000.00

*Control and catalyzed propellants were made twice. The first mix did not process satisfactorily.

Tables 4 through 8 are computer print-outs of a least squares fit of strand burn rate data. The data point at each pressure represents a simple average of at least four tests. Reduced data are plotted in Fig. 18 through 20.

TABLE 4

LEAST SQUARES FIT OF BURNING RATE DATA

ON PROPELLANT CONTROL 1A

```
[illegible]
[illegible] VALUE [illegible] PRESSURE IS ?1000
[illegible] VALUES OF [illegible] AND [illegible] ARE ?100,.017
?[illegible],.[illegible]
?[illegible],.[illegible]
?[illegible],.[illegible]
?[illegible],.[illegible]
?[illegible],.1[illegible]1
?[illegible],.11[illegible]
?1500,.13[illegible]
[illegible]
```

MEASURED DATA		CALCULATED DATA
[illegible]	[illegible]	[illegible]
1[illegible]	.017	.101[illegible]5[illegible]
[illegible]	.[illegible]32	.111[illegible]1
300	.033	[illegible].[illegible]1[illegible]4[illegible]-[illegible]
[illegible]	.[illegible]	[illegible].[illegible]1[illegible]-[illegible]
[illegible]	.[illegible]	[illegible].[illegible]3457-[illegible]
1000	.101	.1[illegible]1
1[illegible]00	.11[illegible]	.1[illegible]3264
15[illegible]	.1[illegible]	.1[illegible]1397

```
[illegible] = [illegible]
[illegible]    = .[illegible]46
[illegible]    = [illegible].5[illegible]1[illegible]-[illegible]
[illegible]500 = 5.7[illegible]-[illegible]
[illegible]1000 = [illegible].1[illegible]-[illegible]
[illegible]1500 = .1[illegible]1[illegible]
[illegible]    = [illegible].[illegible]47[illegible]-[illegible]
[illegible]    = [illegible].7[illegible]

[illegible] : 1.[illegible]   [illegible] : [illegible]
```

TABLE 5

LEAST SQUARES FIT OF BURN RATE DATA

ON PROPELLANT 3, CATALYZED

```
YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
YOUR VALUES OF PRESSURE AND RATE ARE ?100,0.026
 ?200,0.041
 ?500,.072
 ?800,.099
 ?1000,.111
 ?1500,.148
 ?0,0
```

MEASURED DATA		CALCULATED DATA
PRESSURE	RATE	RATE AT 1000
100	.026	.112651
200	.041	.114252
500	.072	.111949
800	.099	.114115
1000	.111	.111
1500	.148	.114323

```
NO OF POINTS= 6
SLOPE       =  .636763
A           =  1.38978E-3
R500        =  7.27028E-2
R1000       =  .113041
R1500       =  .146341
STD. DEV.   =  1.30816E-3
PCT OF MEAN=  1.23526

RUNNING TIME:     1.3 SECS   I/O TIME :     3.0 SECS
```

TABLE 6

LEAST SQUARES FIT OF BURN RATE DATA

ON PROPELLANT 4, CATALYZED

```
RUNNH
YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
YOUR VALUES OF PRESSURE AND RATE ARE ?3
DELETED
 ?100,.022
 ?200,.037
 ?300,.048
 ?500,.063
 ?800,.098
 ?1000
.113

WHAT ?

INCORRECT FORMAT --RETYPE
 ?1000,.113
 ?1200,.131
 ?1500,.157
 ?0,0
```

MEASURED DATA		CALCULATED DATA
PRESSURE	RATE	RATE AT 1000
100	.022	.116021
200	.037	.118287
300	.048	.114504
500	.063	.103925
800	.098	.115135
1000	.113	.118
1200	.131	.11484
1500	.157	.11715

```
NO OF POINTS= 8
SLOPE       =  .722114
A           =  7.81674E-4
R500        =  6.95007E-2
R1000       =  .114648
R1500       =  .153647
STD. DEV.   =  4.59583E-3
PCT OF MEAN=  4.00864


RUNNING TIME:     2.1 SECS    I/O TIME :     3.9 SECS
```

TABLE 7

LEAST SQUARES FIT OF BURN RATE DATA

ON PROPELLANT 5, CONTROL

```
RUNNH

YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
YOUR VALUES OF PRESSURE AND RATE ARE ?100,.022
 ?200,.035
 ?300,.045
 ?500,.059
 ?800,.077
 ?1000,.085
 ?1200,.093
 ?1500,.113
 ?0,0
```

MEASURED DATA		CALCULATED DATA
PRESSURE	RATE	RATE AT 1000
100	.022	8.37733E-2
200	.035	8.91144E-2
300	.045	9.05398E-2
500	.059	8.82379E-2
800	.077	8.76526E-2
1000	.085	.085
1200	.093	8.36573E-2
1500	.113	8.92946E-2

```
NO OF POINTS= 8
SLOPE       =  .580683
A           =  1.57791E-3
R500        =  5.82545E-2
R1000       =  .087123
R1500       =  .110252
STD. DEV.   =  2.66211E-3
PCT OF MEAN=   3.05558


RUNNING TIME:     1.9 SECS    I/O TIME :     3.6 SECS
```

TABLE 8

LEAST SQUARES FIT OF BURN RATE DATA

ON PROPELLANT 5, CATALYZED

RUNNH

YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
YOUR VALUES OF PRESSURE AND RATE ARE ?200,.028
?300,.036
?500,.051
?800,.069
?1000,.078
?1200,.087
?1500,.099
?0,0

MEASURED DATA		CALCULATED DATA
PRESSURE	RATE	RATE AT 1000
200	.028	7.74177E-2
300	.036	7.70392E-2
500	.051	7.90301E-2
800	.069	7.94487E-2
1000	.078	.078
1200	.087	7.75326E-2
1500	.099	7.66236E-2

NO OF POINTS= 7
SLOPE = .631905
A = 9.89977E-4
.500 = 5.02478E-2
.1000 = 7.78644E-2
.1500 = .100603
STD. DEV. = 1.03419E-3
PCT OF MEAN= 1.32819

RUNNING TIME: 1.2 SECS I/O TIME : 3.1 SECS

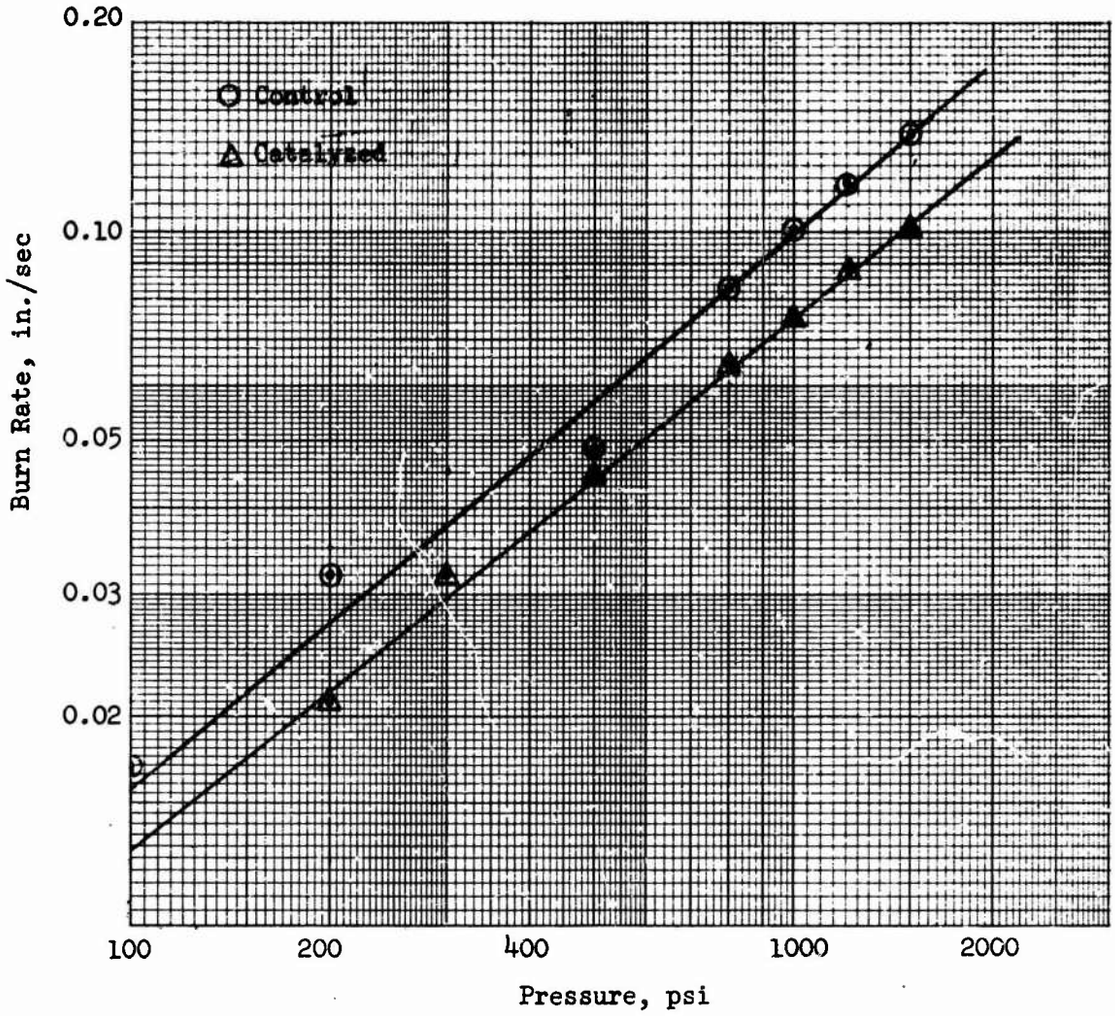

Figure 18. Crawford Bomb Burn Rate Data vs Pressure for Propellants 1A, Control, and 1, Catalyzed*

Figure 18 shows some scatter in data but shows that ammonium chloride reduces the burn rate of an ammonium dichromate catalyzed propellant in the same manner that it reduced the burn rate of an iron catalyzed propellant (milori blue) as shown in the last report.

*Composition presented in first 6-month report. Propellant contains AD and AC catalyst.

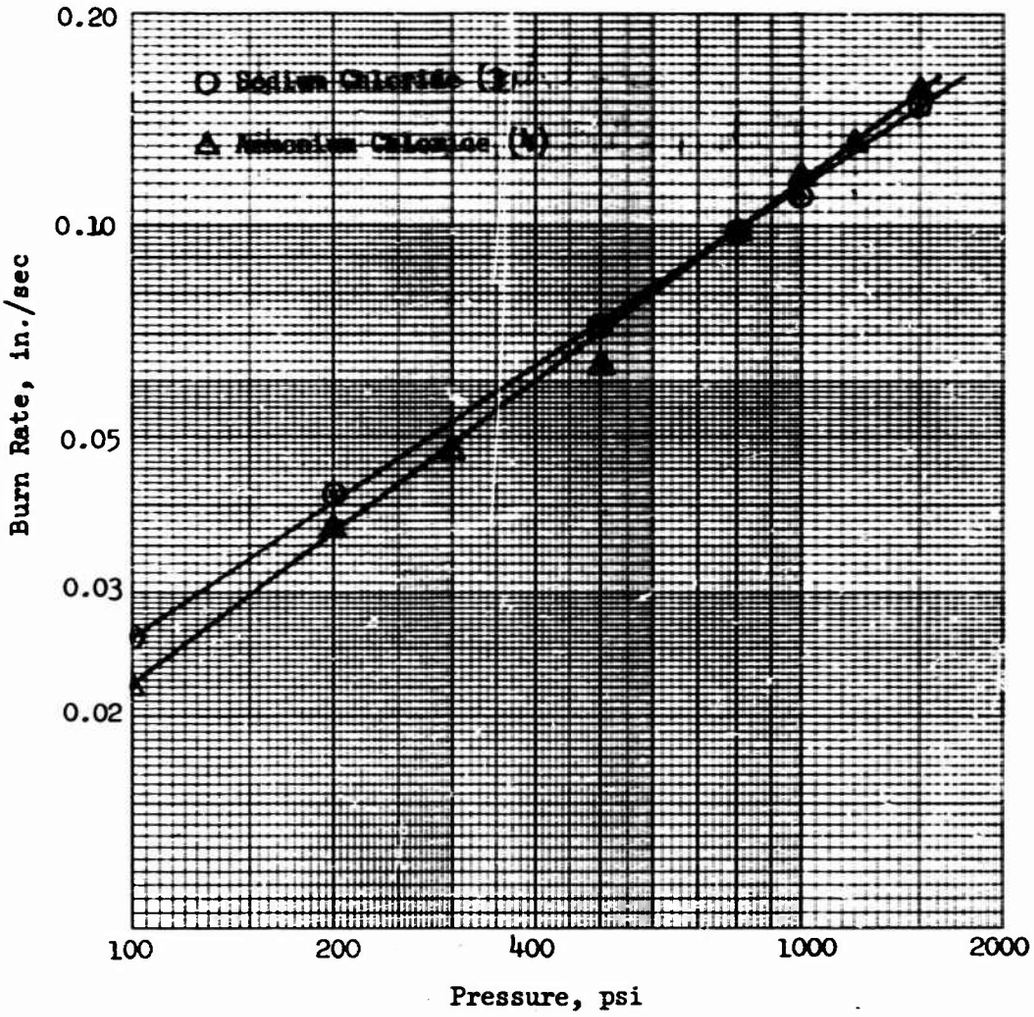

Figure 19. Crawford Bomb Burn Rate Data vs Pressure for Propellants 3 and 4

Figure 19 shows the results obtained from propellants 3 and 4, which contain sodium chloride and ammonium chloride, respectively. The difference between the effects of these two salts is hardly significant. Even though Keenan's results indicated that the cation of the chloride salt was not important, it was considered necessary to demonstrate this in a propellant.

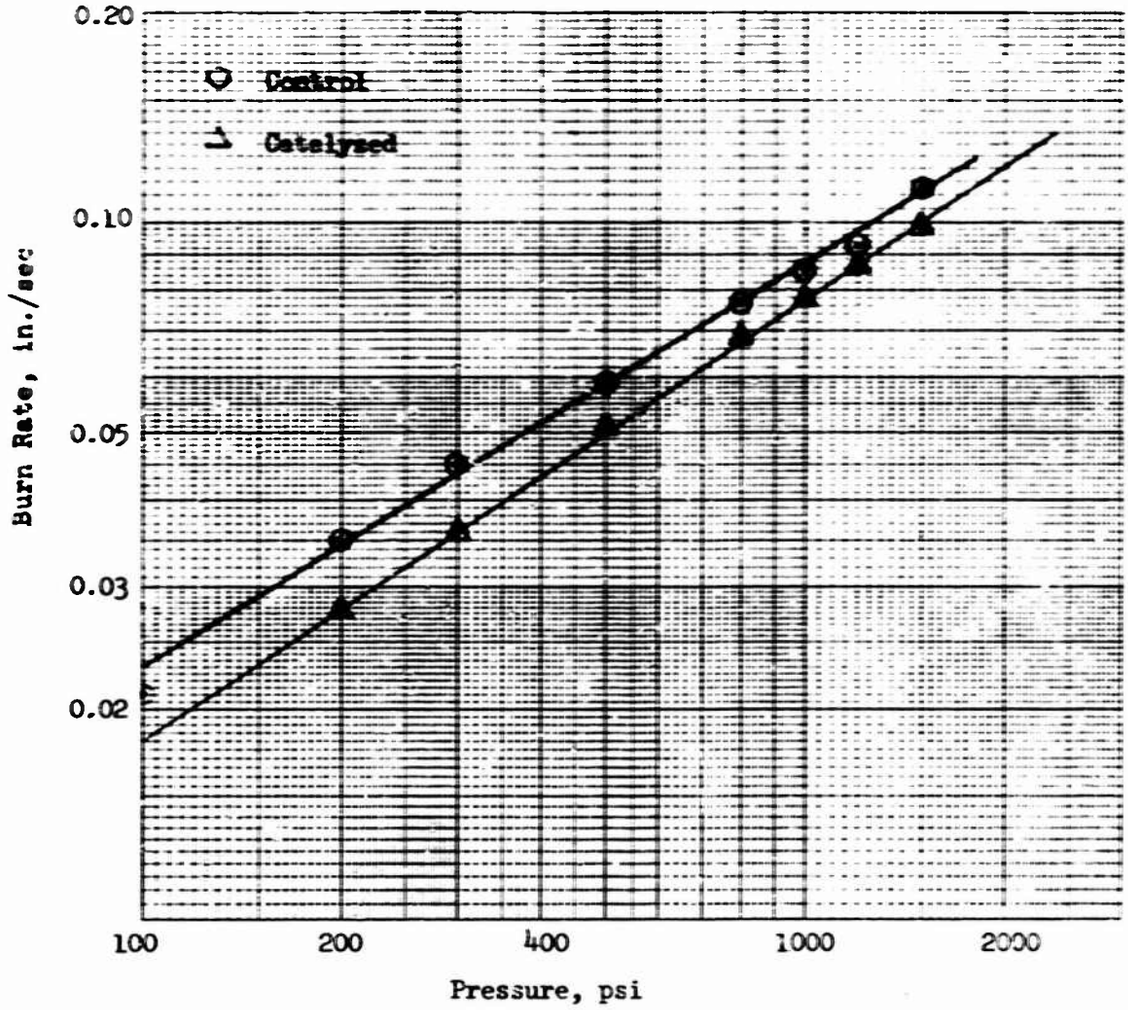

Figure 20. Crawford Bomb Burn Rate Data vs Pressure for Propellants 5, Control, and 5, Catalyzed

Propellant 5 was made to check the effect of the chromium/chloride system in the absence of all other metals (see Fig. 20). All propellants made previously contained magnesium oxide at about a 0.5% level as a part of the propellant cure system. Propellant 5 uses 1,4-bis (trichloromethyl)-benzene as a quaternary curing agent. The difference between propellants 3 and 5 do not appear great. Propellant 5 shows a significantly lower slope of the burn rate vs pressure curve and less depression of burn rate by the chloride at higher pressures.

PROPELLANT MIXES (AMMONIUM PERCHLORATE)

Compositions of castable ammonium perchlorate propellants that have been made are given in Table 9. The oxidizer and catalyst ingredients were thoroughly blended before they were added to the propellant binder. Computer runs are given in Tables 9 through 13, and the resulting data are plotted in Fig. 21 and 22. Prepellant 6 containing ammonium chloride showed a depression in burn rate at low pressures; however, the magnitude of the depression is barely significant.

TABLE 9

COMPOSITION OF AMMONIUM PERCHLORATE PROPELLANTS

Propellant	Ingredients	Wt %	Actual Weight Used, grams
Control 6	Binder	14.00	63.00
	AP (200 micron)	59.79	269.06
	AP (20 micron)	25.63	115.34
	Ammonium Dichromate	0.58	2.60
			450.00
Catalyzed 6	Binder	14.00	63.00
	AP (200 micron)	57.27	257.72
	AP (20 micron)	25.63	115.34
	Ammonium Dichromate	0.58	2.61
	Ammonium Chloride	2.52	11.34
			450.01
Control 7	Binder	14.00	63.00
	AP (200 micron)	51.25	230.63
	AP (20 micron)	25.63	115.34
	Ammonium Dichromate	0.58	2.61
	Ammonium Nitrate	8.54	38.43
			450.01
Catalyzed 7	Binder	14.00	63.00
	AP (200 micron)	48.73	219.29
	AP (20 micron)	25.63	115.33
	Ammonium Dichromate	0.58	2.61
	Ammonium Nitrate	8.54	38.43
	Ammonium Chloride	2.52	11.34
			450.00

TABLE 10

LEAST SQUARES FIT OF BURN RATE DATA

FROM PROPELLANT 6, CONTROL

```
READY
RUNNH
YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
YOUR VALUES OF PRESSURE AND RATE ARE ?100,.137
 ?200,.189
 ?300,.220
 ?500,.267
 ?800,.326
 ?1000,.357
 ?1200,.398
 ?1500,.416
 ?0,0
```

MEASURED DATA		CALCULATED DATA
PRESSURE	RATE	RATE AT 1000
100	.137	.353459
200	.189	.366581
300	.22	.361118
500	.267	.355157
800	.326	.357361
1000	.357	.357
1200	.398	.369225
1500	.416	.352055

```
NO OF POINTS= 8
SLOPE       =  .411618
A           =  2.09015E-2
R500        =  .26985
R1000       =  .358948
R1500       =  .424145
STD. DEV.   =  6.17475E-3
PCT OF MEAN=  1.72023

RUNNING TIME:     1.4 SECS    I/O TIME :     3.7 SECS

READY
BYE

OFF AT 14:11
```

TABLE II

LEAST SQUARES FIT OF BURN RATE DATA

FROM PROPELLANT 6, CATALYZED

```
READY
RUNNH
YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
YOUR VALUES OF PRESSURE AND RATE ARE ?100,.132
 ?200,.178
 ?300,.210
 ?500,.265
 ?800,.310
 ?1000,.343
 ?1200,.374
 ?1500,.404
 ?0,0

PRESSURE        RATE            RATE AT 1000
 100             .132            .341144
 200             .178            .345661
 300             .21             .345013
 500             .265            .352679
 800             .31             .339879
 1000            .343            .343
 1200            .374            .346913
 1500            .404            .341797


NO OF POINTS= 8
SLOPE       =  .412364
A           =  1.99565E-2
R500        =  .258846
R1000       =  .34449
R1500       =  .407183
STD. DEV.   =  4.07968E-3
PCT OF MEAN=  1.18427


RUNNING TIME:    2.4 SECS   I/O TIME :    3.2 SECS

READY
BYE

OFF AT 09:01
```

TABLE 12

LEAST SQUARES FIT OF BURN RATE DATA

FROM PROPELLANT 7, CONTROL

```
RUNNH
YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
YOUR VALUES OF PRESSURE AND RATE ARE ?100,.127
 ?200,.166
 ?300,.200
 ?500,.249,-
 ?800,.305
 ?1000,.341
 ?1200,.368
 ?1500,.407
 ?0,0

PRESSURE        RATE            RATE AT 100C
 100             .127            .344832
 200             .166            .333675
 300             .2              .337176
 500             .249            .336347
 800             .305            .336
 1000            .341            .341
 1200            .368            .340016
 1500            .407            .341354


NO >POINTS= 8
SLOPE       =  .433803
A           =  1.69243E-2
R500        =  .250804
R1000       =  .338783
R1500       =  .403934
STD. DEV.   =  3.62497E-3
PCT OF MEAN=  1.07


RUNNING TIME:     1.7 SECS    I/O TIME :     2.5 SECS

READY
BYE

OFF AT 07:36
```

TABLE 13

LEAST SQUARES FIT OF BURN RATE DATA

FROM PROPELLANT 7, CATALYZED

```
READY
RUNNH
YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
YOUR VALUES OF PRESSURE AND RATE ARE ?100,.116
 ?200,.154
 ?300,.188
 ?500,2-.240
 ?800,.300
 ?1000,.338
 ?1200,.369
 ?1500,.403
 ?0.0,0.0

PRESSURE        RATE            RATE AT 1000
 100             .116            .34199
 200             .154            .327888
 300             .188            .330886
 500             .24             .332324
 800             .3              .333139
 1000            .338            .338
 1200            .369            .338724
 1500            .403            .333135


NO OF POINTS= 8
SLOPE       =  .469556
A           =  1.30529E-2
R500        =  .241559
R1000       =  .334483
R1500       =  .40463
STD. DEV.   =  4.65096E-3
PCT OF MEAN=   1.39049


RUNNING TIME:    2.3 SECS   I/O TIME :    3.4 SECS

READY
BYE

OFF AT 09:01
```

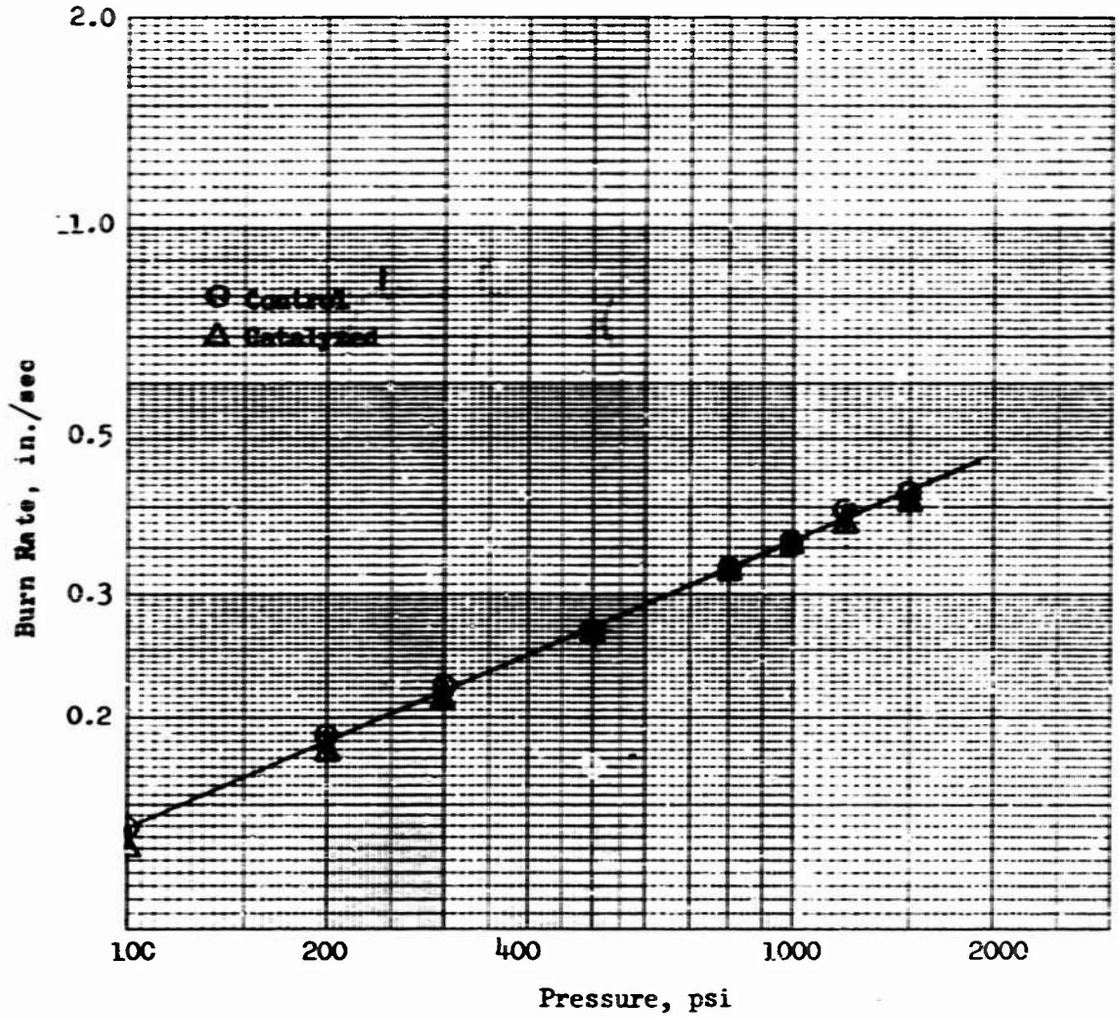

Figure 21. Crawford Bomb Burn Rate Data vs Pressure for Propellants 6, Control, and 6, Catalyzed

Propellant 7 contained the catalyst system and ammonium nitrate. Again, there was a slight depression in burn rate due to the addition of chloride (see Fig. 22). A comparison of controls 6 and 7 indicates the depression due to the ammonium nitrate. It is important to note that 2.5% ammonium chloride is a better burn rate depressant than 8.5% ammonium nitrate.

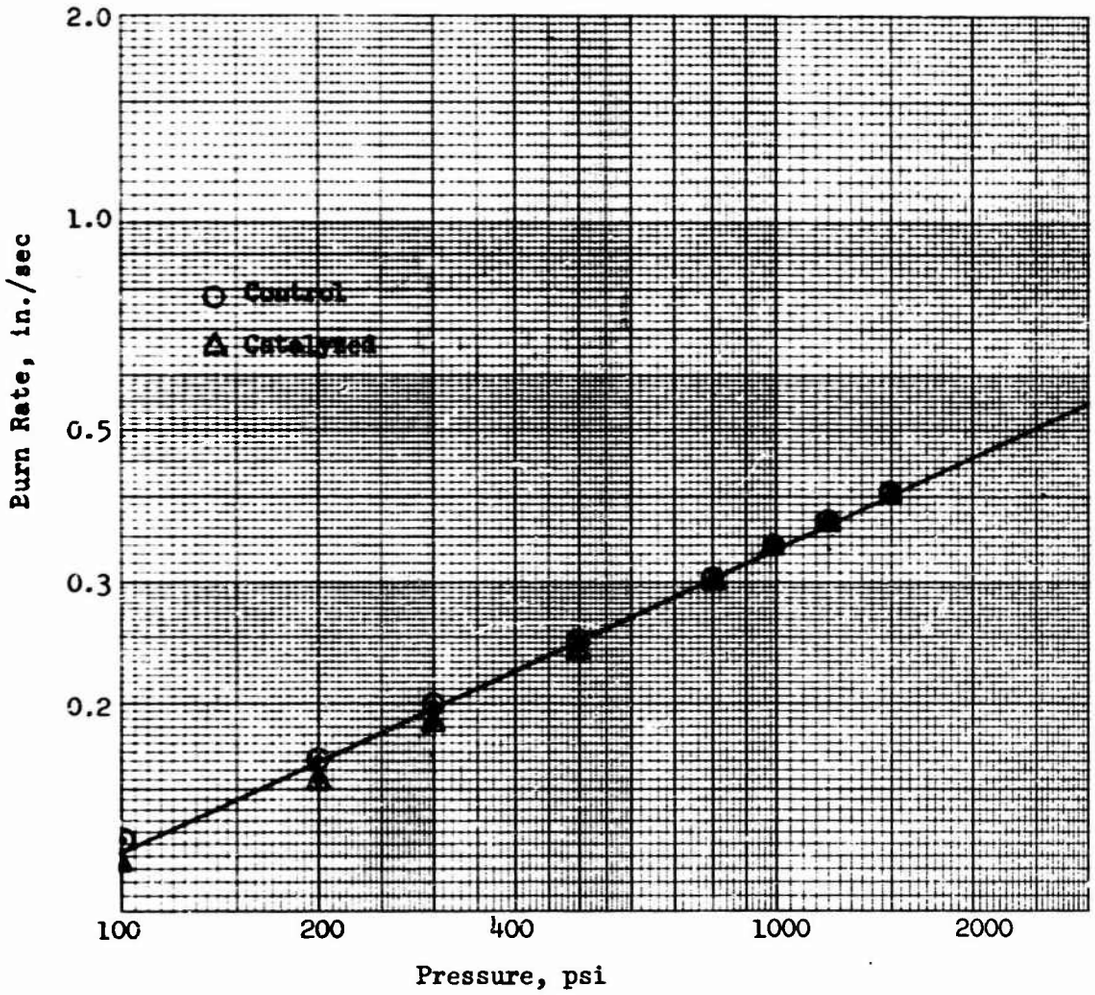

Figure 22. Crawford Bomb Burn Rate Data vs Pressure for Propellants 7, Control, and 7, Catalyzed

DYNAMIC DSC (PROPELLANTS)

Six of the ammonium nitrate propellants made thus far were studied by DSC (Fig. 23 through 28). Dynamic thermograms were run at several heating rates. Agreement between thermograms of these actual propellants and the micromixed pseudo-propellants was exceptionally good.

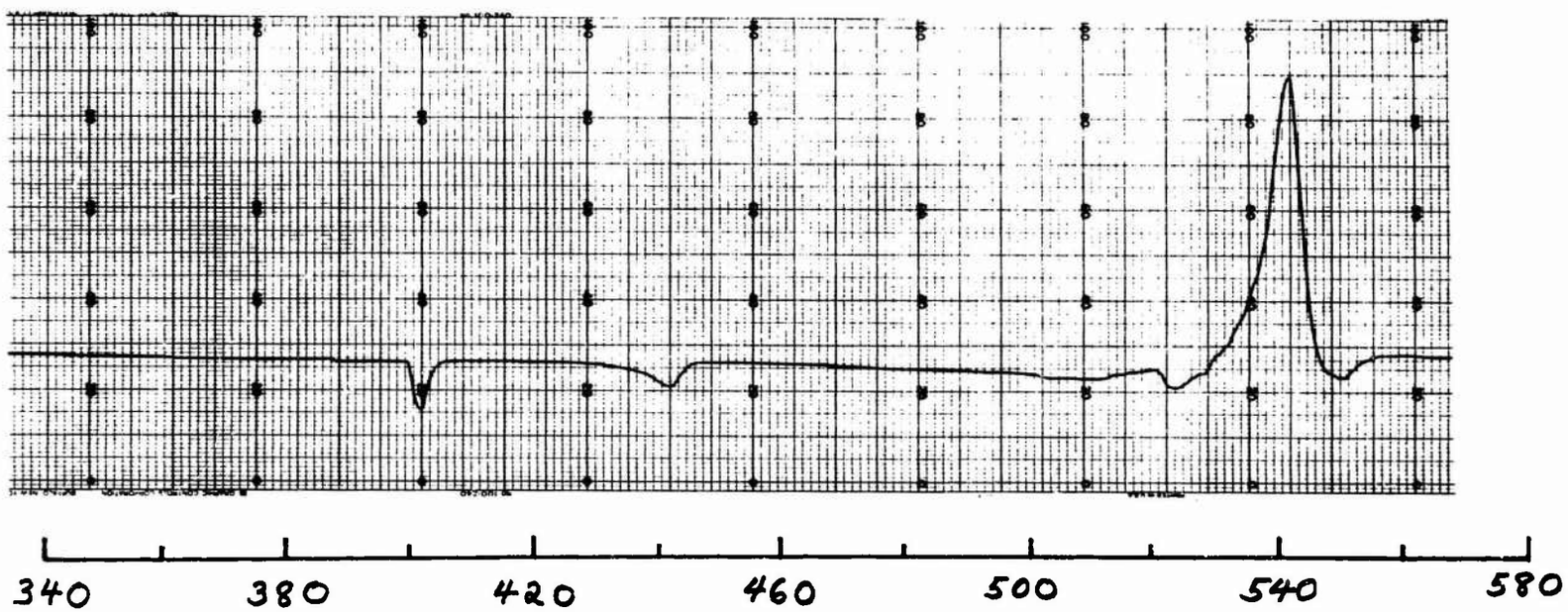

Figure 23. DSC Thermogram of Propellant 1, Control, at 20 deg/min (Sample Weight 3.13 milligrams)

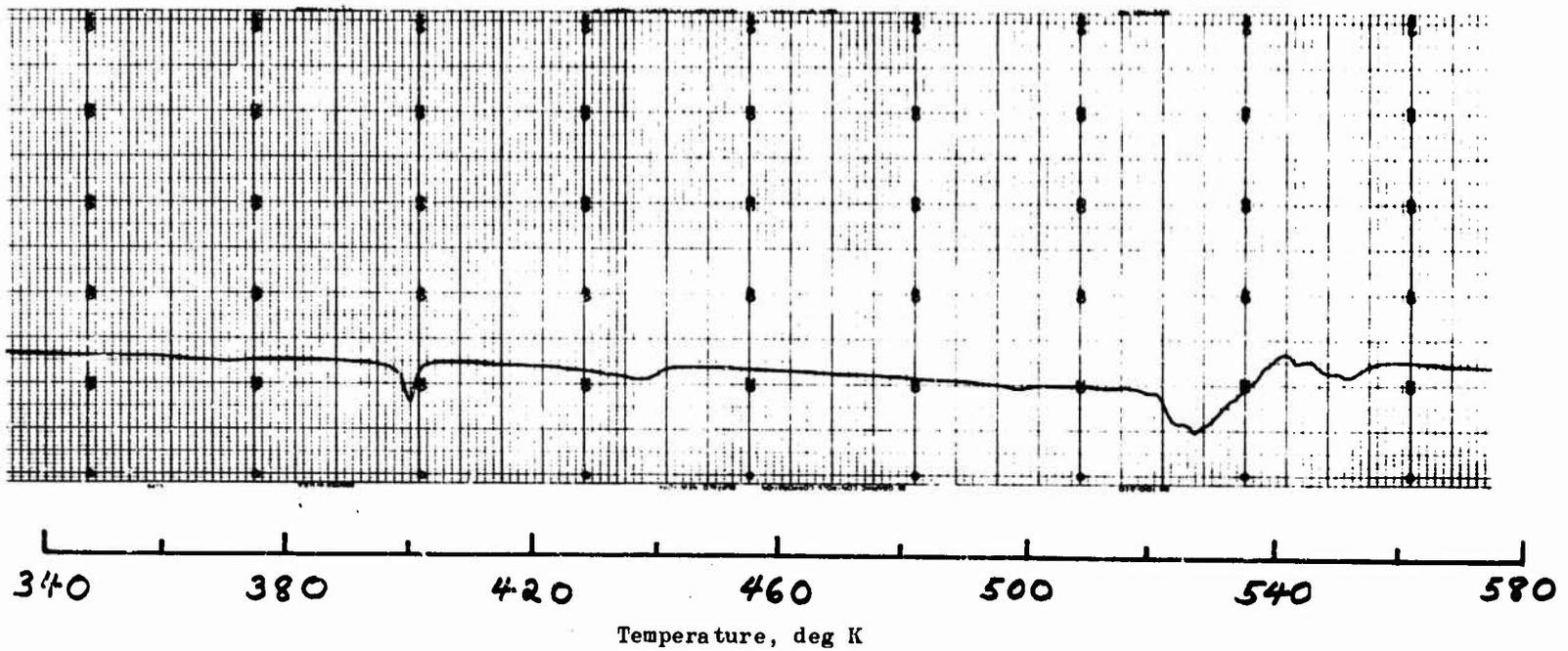

Figure 24. DSC Thermogram of Propellant 1, Catalyzed, at 20 deg/min (Sample Weight 3.22 milligrams)

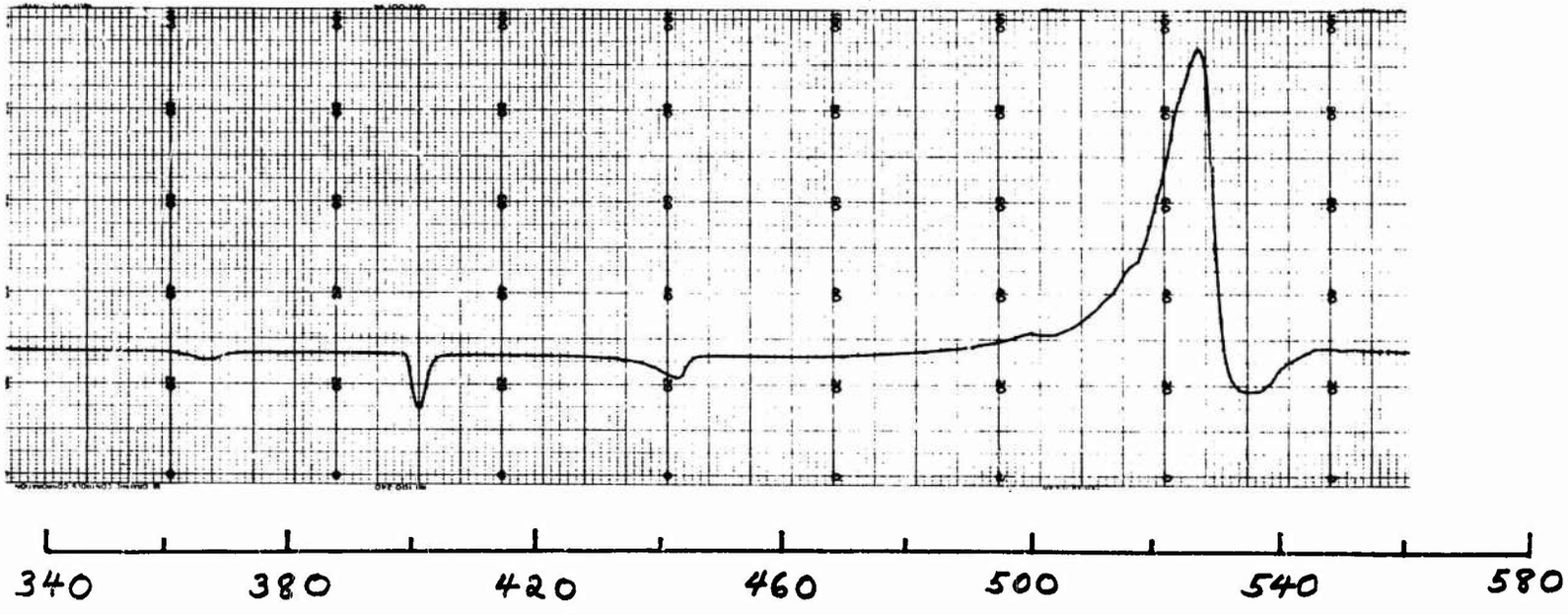

Figure 25. DSC Thermogram of Propellant 2, Control, at 20 deg/min (Sample Weight 3.20 milligrams)

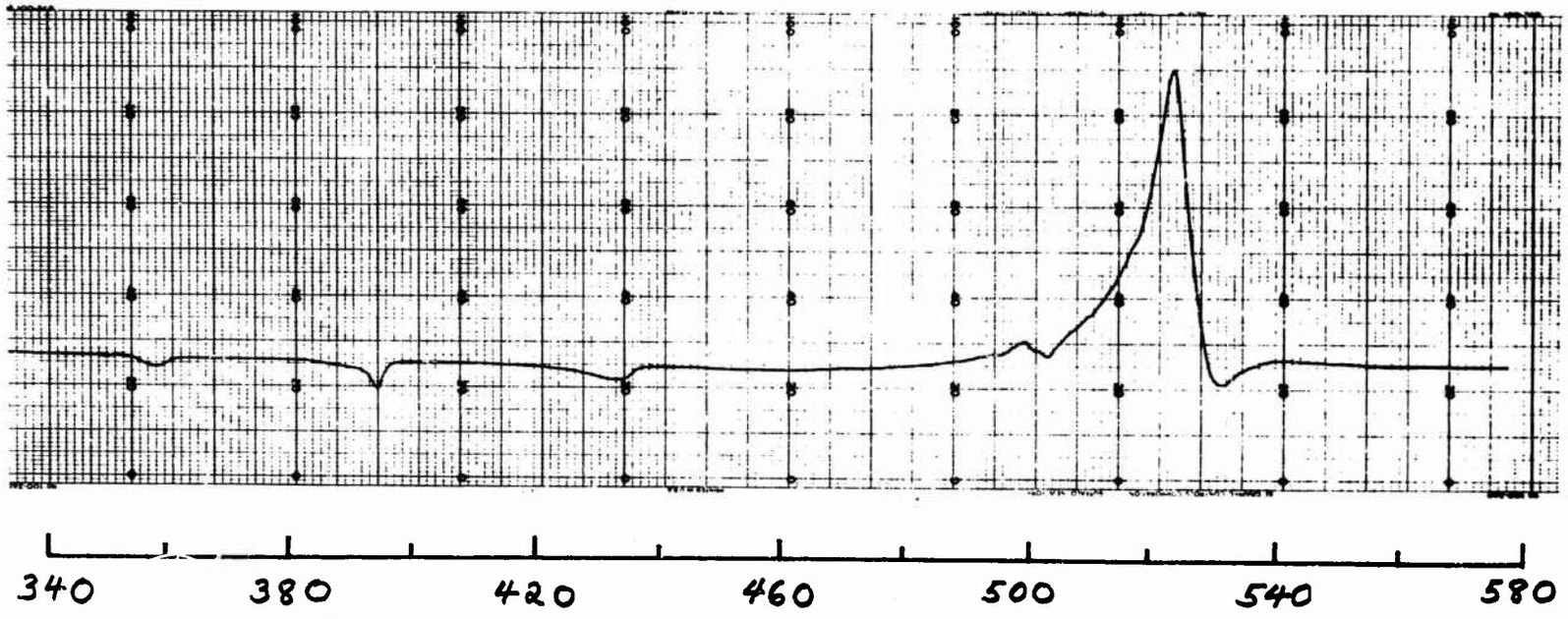

Figure 26. DSC Thermogram of Propellant 2, Catalyzed, at 20 deg/min (Sample Weight 3.28 milligrams)

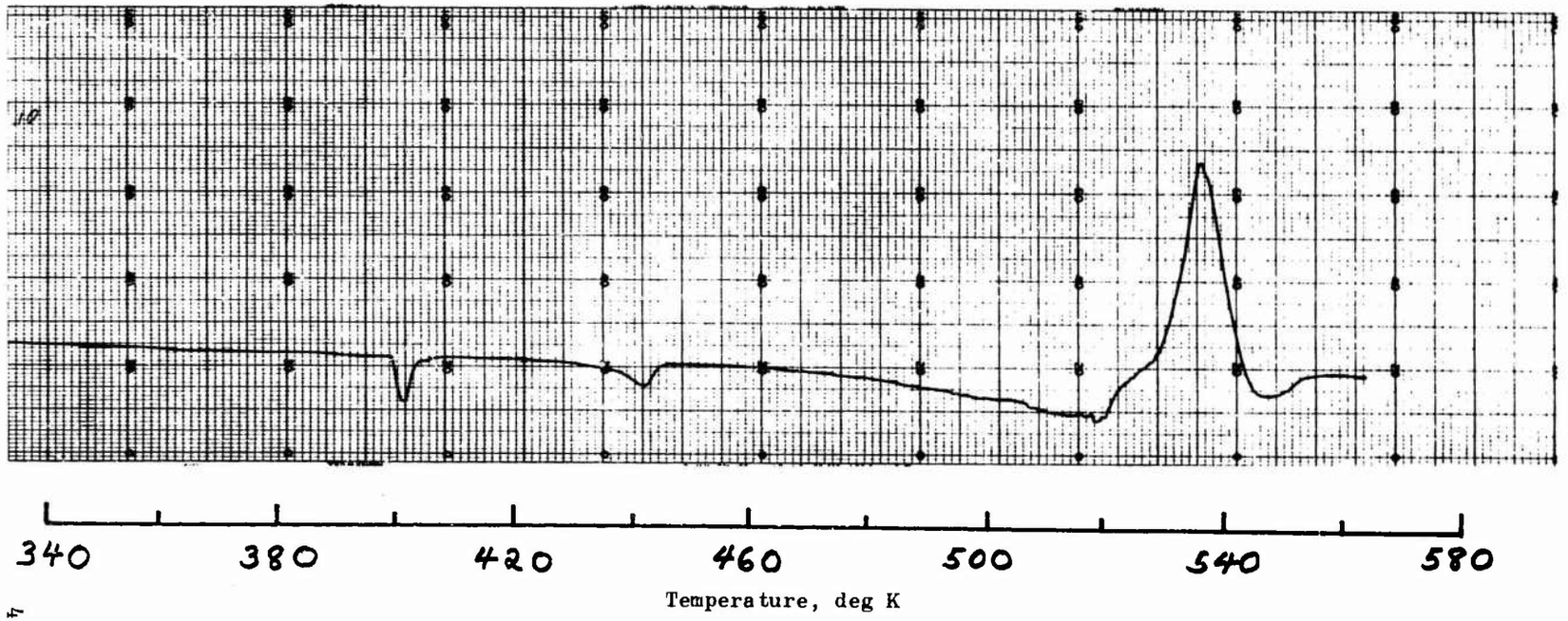

Figure 27. DSC Thermogram of Propellant 1A, Control, at 20 deg/min (Sample Weight 3.07 milligrams)

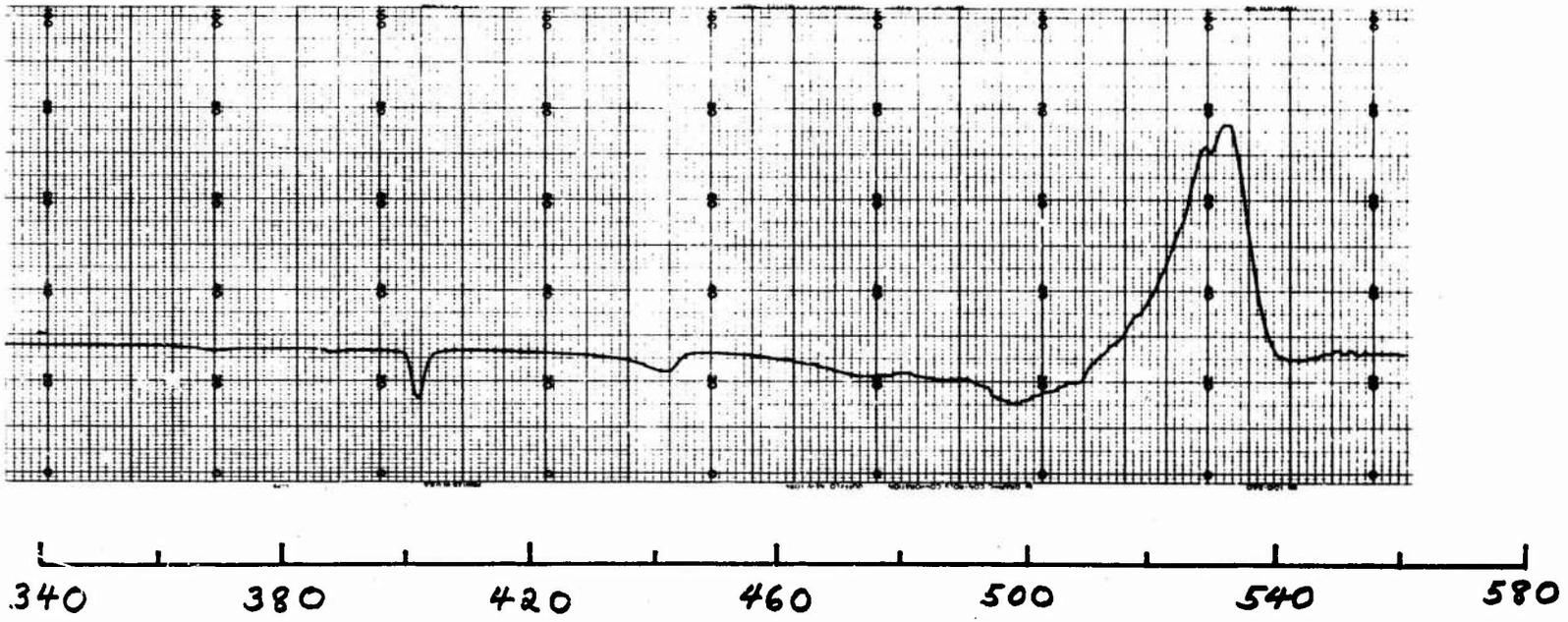

Figure 28. DSC Thermogram of Propellant 4, Catalyzed, at 20 deg/min (Sample Weight 3.39 milligrams)

One of the most significant effects of the catalyst system is shown in Fig. 23 and 24. At a heating rate of 20 deg/min, the exotherm shown in propellant 1, control, is totally suppressed by the addition of the chromium/chloride catalyst system. Figures 25 and 26 show a much smaller reduction with the iron/chloride system.

CO-CRYSTALLIZATION

The melt procedure used by Keenan for the preparation of catalyzed oxidizer is not very practical or safe for the preparation of large quantities (1000 grams) for propellant mixes. Therefore, some time was spent attempting to prepare a co-crystalline ammonium nitrate/ammonium chloride that contained at least 2.5% ammonium chloride.

The general procedure for co-crystallization was as follows:

> 200 ml of methanol (reagent grade absolute) was brought to boiling in a 500 cc Erlenmeyer flask. 2.75 grams of ammonium chloride (ACS reagent) was dissolved and then 0.18 grams of ammonium dichromate (reagent grade) was dissolved. An additional 200 ml of methanol was added as necessary to maintain solution as 97.1 grams of ammonium nitrate (propellant grade) was added. This solution was allowed to cool to room temperature and then placed in a -15 F freezer overnight. The crystals were then filtered, washed with ether, and dryed by suction.

Observation of the crystals showed the chromium to be reduced to chromic oxide and present as separate crystals that could be physically separated by shaking the mixture. An analysis of the upper white crystals showed only a trace of chromium and 0.12% chloride. A number of additional attempts were made to co-crystallize ammonium nitrate and ammonium chloride without the dichromate. In all cases, regardless of the original concentration, the first crop of crystals contained 0.15% or less chloride. A second crop of crystals of higher chloride content could be obtained by adding ether to the mother liquor. The first crop

appeared on microscopic examination to be an isomorphous mixed crystal and the second crop had the appearance of a polymorphous crystal mixture. No more work is planned with ammonium nitrate co-crystallization, but at least one propellant mix is planned with the co-crystallized ammonium nitrate containing 0.15% chloride.

A procedure for co-crystallization of ammonium perchlorate and potassium chloride is already available, and a mixed crystal can be obtained with as much as 10% KCl. Preparation of a sample of AP containing about 2.5% KCl is planned.

CONCLUSIONS

Strand burning rates are continuing to verify the prediction of a burn rate depression by chloride. This prediction was made on the interpretation of DSC data and assuming the importance of condensed phase heat release. Ammonium dichromate is known to be a good burn rate catalyst for ammonium nitrate, but there is no precise knowledge as to how it functions. Gas phase proponents (now dwindling in number) suggest that it functions in the gas phase only. This work does not support that view. The ammonium dichromate catalyzed propellants show a larger exothermic decomposition than propellants without ammonium dichromate, and this exotherm is greatly suppressed by chloride. Suppression of the burn rate of ammonium dichromate catalyzed propellant by chloride represents an indirect support for activity of the catalyst in the condensed phase.

Isothermal TGA showed no induction time with the synergistic decomposition catalyst and a relatively constant rate of decomposition at each temperature studied. It appears that the induction time observed by Keenan was actually a self-heating time. The rate of decomposition at 195 degrees is relatively slow. Keenan used a 195 degree furnace temperature for most of his runs and a relatively large sample (6 grams).

The ammonium nitrate/catalyst mixture has a relatively low thermal conductivity which means that if heat is generated within a sample of any size it is likely to be generated faster than it can be conducted out of the sample, thus leading to the phenomena called self-heating. In this effect the internal temperature of the sample can become run-away. It is likely that the nitrogen sparge which Keenan used to delay the induction time (self-heating) was actually in effect only carrying heat away from the sample convectively so that the sample did not reach a high enough temperature to decompose rapidly.

The DSC and DTA work with micro samples have led us to the conclusion that most of the heat release in the sample is in the gas phase and not the condensed phase. The larger the sample, the more self-heating that would occur because of the vigorous bubbling of the liquid sample from decomposition gases. The micro samples do not have enough contact with the gas phase to absorb its heat.

Propellants made with a quaternary type cure gave essentially the same results as the more normally used cure system containing magnesium oxide.

FUTURE PLANS

During the next 6 months 15 to 20 propellant mixes are planned. These mixes will include a nitrate mix for determination of temperature sensitivity by burning strands at -70, 77 and 170 F, a nitrate mix with co-crystallized AN/AC (0.15% chloride), castable mix with co-crystallized AP/KCl (2.5% KCl), and a nitrate mix with a melt of AN/AC. A number of castable ammonium perchlorate mixes are planned to evaluate the effect of ammonium chloride and potassium chloride on known catalysts such as iron oxide or copper chromite.